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Activities of the NBS Spectrochemical Analysis Section

July 1970 to June 1971

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Activities of the NBS Spectrochemical Analysis Section July 1970 to June 1971

K. F. J. Heinrich and S. D. Rasberry

Institute for Materials Research
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Washington, D.C. 20234



NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.

FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963, and became part of the Institute for Materials Research in the February 1, 1964, reorganization. It consists at present of nine Sections and about 100 technical personnel encompassing some 45 different analytical competences from activation analysis to x-ray spectroscopy. These competences, and in turn the Sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it standard reference material or service analysis. In addition it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is a highly important output of our laboratories. In addition, however, it has been our experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information about our programs. A word is perhaps in order about the philosophy of these yearly progress reports. In any research program a large amount of information is obtained and techniques developed which never find their way into the literature. This includes the "negative results" which are so disappointing and unspectacular but which can often save others considerable work. Of importance also are the numerous small items which are often explored in a few days and which are not important enough to warrant publication -- yet can be of great interest and use to specialists in a given area. Finally there are the experimental techniques and procedures, the designs and modifications of equipment, etc., which often require months to perfect and yet all too often must be covered in only a line or two of a journal article.

Thus our progress reports endeavor to present this information which we have struggled to obtain and which we feel might be of some help to others. Certain areas which it appears will not be treated fully in regular publications are considered in some detail here. Other results which are being written up for publication in the journal literature are covered in a much more abbreviated form.

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1971 we plan to issue these summaries for all of our Sections. The following is the seventh annual report on progress of the Spectrochemical Analysis Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

The seventh annual progress report of the Spectrochemical Analysis Section covers a period of intense evolution. The current trend towards increasingly complex and sophisticated analytical tools is reflected in the prospects of the Ion Probe Mass Analyzer; the installation of the Division Computer System will accelerate the already existing trend towards automatic experiment programming and data handling. However, the human and financial resources of the Section are limited; hence, a continuing process of reevaluation of priorities is required. The potentials and limitations of new tools must be explored in order to insure their rational utilization; at the same time, we must give full use to established techniques which continue to render valuable services.

On January 11, 1971, Mr. B. F. Scribner, who had been in charge of this Section since its inception, left it to assume the position of Deputy Division Chief. It is a difficult task for his successors to maintain the high levels of efficiency established by him.

This report reviews the progress in research, instrumentation, and service activities of the Section for the past year. In order to specify procedures adequately, it has been necessary occasionally to identify commercial materials and equipment. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

Kurt F. J. Heinrich, Acting Chief
Spectrochemical Analysis Section

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TABLE OF CONTENTS

	<u>PAGE</u>
ABSTRACT	1
1. INTRODUCTION	3
A. Changes in Facilities	3
B. Personnel and Activities	5
2. OPTICAL SPECTROSCOPY	8
A. Research	8
B. Applications to Analysis	8
1. Analyses of Standard Reference Materials	8
2. Other Service Analyses	10
C. Description of Homogeneity Testing Method	13
D. Modification of Gas-Sheath Arc Unit	16
3. X-RAY FLUORESCENCE SPECTROMETRY	20
A. Instrumentation	20
B. Computations for Quantitative Analysis	22
C. Characterization of Standard Reference Materials	27
1. Preliminary Testing	27
2. Homogeneity Testing	28
3. Certification of Composition	30
4. Utility of Standard Reference Materials	30
5. Production Quality Control	31
D. Service Analyses	31
E. Investigation for Special Applications	33
F. Other Applications	34
4. ELECTRON PROBE MICROANALYSIS	35
A. Instrumental Improvements	35
1. Scan Driver	35
2. Electron Lens and Power Supplies for Higher Beam Resolution	42
3. Residual Gas Analyzer (RGA)	42

B.	Scanning Techniques and Sample Preparation for Small Particles and Biological Thin Cuts . . .	45
1.	Handling of Particles	46
2.	Analysis of Biological Specimens	49
C.	Quantitative Analysis	53
1.	Limit of Detection	54
2.	Further Measurements on Standard Reference Materials	56
3.	Computer Programs	57
4.	Studies on Binary Alloys	60
D.	Service Analyses	62
5.	PRECONCENTRATION TECHNIQUES	64
A.	Interaction of Nitrilotriacetic Acid (NTA) Solution with River Sediments	64
B.	Orchard Leaves, Standard Reference Material 1571	68
1.	Determination of Fe, Pb, Zn, Cu, Ni, and Se	68
2.	Determination of Mercury	70
6.	LIST OF PERSONNEL AND ACTIVITIES	73
A.	Personnel	73
B.	Publications	74
C.	Talks Given	75
D.	Committee Activities	78
7.	ACKNOWLEDGMENTS	80
8.	LIST OF REFERENCES	82
APPENDIX A:	CERTIFICATES FOR NBS STANDARD REFERENCE MATERIALS RECENTLY ISSUED	86
1.	SRM 1261 AISI 4340 Steel	87
2.	SRM 1262 AISI 94B17 Steel (Modified)	90
3.	SRM 1263 Cr-V Steel (Modified)	93
4.	SRM 1264 High-Carbon Steel (Modified)	96
5.	SRM 1265 Electrolytic Iron	99
6.	SRM 483 Fe-3Si Alloy Microprobe Standard	102
7.	SRM 485 Austenite in Ferrite	103

8.	SRM's 1206-2, 1207-1, 1207-2, 1208-1, 1208-2 High-Temperature Alloys: René 41, Waspaloy, and Inco 718	105
9.	SRM 1134 High-Silicon Steel	107
10.	SRM 1623 Sulfur in Residual Fuel Oil	109
11.	SRM 1624 Sulfur in Distillate Fuel Oil	110
12.	SRM 654a Titanium Alloy, 6Al-4V	111
13.	SRM 917 D-Glucose	112
14.	SRM 918 Potassium Chloride	113
15.	SRM 984 Rubidium Chloride	114
16.	SRM 1061c Magnesium Cyclohexanebutyrate	115

APPENDIX B:	FUNCTIONAL BLOCK DIAGRAM OF ELECTRON BEAM SCANNING SYSTEM	116
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LIST OF FIGURES

FIGURE NO.

1.	Hardware analyzed for alloy identification	12
2.	Sampling of steel bar for homogeneity studies	13
3.	Time-sequence of measurements for a four-slice by four-spot homogeneity test	16
4.	Computer output for analysis of variance of the phosphorus concentration in cast iron	17
5.	Schematic drawing of the modified gas-sheath arc unit	18
6.	Resolution test for our lithium-drifted sili- con detector	21
7.	A qualitative representation of possible interelement effects	23
8.	Experimental data for the determination of iron in ternary alloys of iron, chromium and nickel	25
9.	Homogeneity test for calcium in Portland Cement	28

FIGURE NO.

10.	Homogeneity test for sulfur in Portland Cement	29
11.	X-ray fluorescence calibration curve for the determination of sulfur in oil	32
12.	X-ray fluorescence calibration curve for the determination of phosphorus in cloth	34
13.	Electromagnetic translation of the field of view	36
14.	Rotation sequence through steps of 180°	37
15.	Normal image and mirror image of same view field	38
16.	Electronic line scan on the same specimen as Fig. 13	39
17.	Y-axis modulation of target current signal with oblique view-field presentation	40
18.	Residual gas analyzer mounted on top of the tank of the electron probe microanalyzer	43
19.	Residual gas spectra of the atmosphere within the tank	44
20.	Diagram of particle mounted within thin organic film	47
21.	Absorbed electron scanning image of fly ash particles mounted in collodion	49
22.	Pulse-height spectra of four fly ash particles mounted on collodion film	51
23.	Schematics of specimen holder for the detection of scattered (transmitted) electrons	52
24.	Scanning transmission electron micrograph of unstained cartilage tissue	53
25.	Cr K α signal from low-alloy steels	55

FIGURE NO.

26.	The copper K α measurements in gold-copper binaries	58
27.	Experimental and theoretical intensity ratios of Cu K α for a nominally Au ₆₀ -Cu ₄₀ alloy . .	59
28.	Apparatus for digestion of organic samples and equilibration of mercury	71

LIST OF TABLES

TABLE NO.

1.	Results for Fe-Ni-Cr alloys using two computation procedures	26
2.	Summary of results for x-ray fluorescence tests of homogeneity of seven new Portland cement Standard Reference Materials	30
3.	Concentrations in micrograms of element per milliliter of solution which had been interacted with river bottom sediment (Pb, Hg, Sn, Cd, Zn, Cu and Fe)	67
4.	Concentrations in micrograms of element per milliliter of solution which had been interacted with river bottom sediment (Ba, Sb, Mo, Sr, Cr, Ni and Ag)	68
5.	Average concentrations in the solution obtained from wet-ashing one-gram samples of Orchard Leaves SRM 1571	70

ACTIVITIES OF THE NBS SPECTROCHEMICAL
ANALYSIS SECTION

July 1970 to June 1971

Edited by K. F. J. Heinrich and S. D. Rasberry

Spectrochemical research activities, improvements in equipment and applications, especially to the certification of NBS Standard Reference Materials, are summarized. In optical emission spectroscopy, studies have been carried out on a modified gas-sheath arc excitation source. Application has been made of this source and several other conventional excitation sources to analytical problems related to both Standard Reference Materials and other materials being investigated at NBS. Newly derived computation procedures for quantitative x-ray fluorescence analysis are described as well as new instrumentation added for x-ray spectrochemical studies. In electron probe microanalysis, research and new instrumentation has been directed to improved detection limits and quantitation; special emphasis has been given to methods for small particles and biological thin cuts. Methods of preconcentration of impurities have been advanced and applied, in some cases at parts per billion (10^{-9}) limits, to water pollution, river sediment specimens. Mercury, cadmium, and lead were among the elements determined. Work on Standard Reference Materials resulted in certification of several special steels, several high temperature alloys, a high-silicon steel and a titanium alloy, among others. Listings are given of 8 publications and 25 talks by members of the Section during the year.

Key words:

Analysis; computer program; electron probe; micro-analysis; optical spectrometry; preconcentration techniques; spectrochemical analysis; Standard Reference Materials; x-ray fluorescence analysis.

1. INTRODUCTION

The programs and aims of the Section, as well as the instrumentation available for its activities, are described in earlier reports of this series [1-6], which will be used as reference in the current report. Copies of the earlier reports are available on request. They contain records of the research activities, publications, talks given, and analytical work. In the present report, we have aimed to maintain the format established by the previous editor, B. F. Scribner, who is now Deputy Chief, Analytical Chemistry Division, NBS.

A. Changes in Facilities

The major equipment of the Section has been listed in last year's report [6]. The only substantial addition to this list is the solid state x-ray detector system for x-ray fluorescence spectrometry analysis, which is described in Section 3 of this report.

An ion microprobe mass analyzer has been purchased and is expected to arrive at NBS in the winter of 1971. This instrument has been acquired jointly with NASA (Goddard Space Flight Center). Since the device will considerably enlarge the research activities and analytical capabilities of this Section, we will briefly describe its characteristics and suggested applications.

The ion microprobe mass analyzer is based on mass spectrometric analysis of secondary ions sputtered from a specimen surface under the impact of a monoisotopic ion beam, focused to a diameter of 1-300 μm . It is thus a tool for elemental and isotopic analysis of a microvolume at the surface of a solid specimen. The basic design of the instrument is analogous to that of the electron probe microanalyzer, with the electron optics replaced by ion optics, and a mass

spectrometer substituting for the x-ray spectrometer. The analogy is completed by the fact that both instruments allow for line and raster scanning of the respective beams.

Compared with the electron probe, the ion microprobe mass analyzer offers several significant advantages:

1. The sensitivity for most elements, particularly those with low atomic numbers, is better by several orders of magnitude.
2. Isotopic ratios can be determined.
3. Since the ions do not appreciably diffuse in depth or laterally, the analysis is essentially of the surface, and the resolution is practically identical with the beam diameter - which can be made to be 1 μm or less.
4. It is not necessary that the specimens be good conductors of heat or electricity.
5. Since there is a choice of positive or negative ions of several elements, the relative sensitivities of elements to be determined can be varied within wide ranges.

The ion microprobe has the following disadvantages:

1. The method is destructive, since the specimen is slowly eroded during the ion bombardment. (This, however, can be turned into an advantage, since variations in concentration can be observed as a function of depth within the specimen.)
2. As the physical process involved is more complex than that of x-ray excitation by electrons, it is anticipated that the accuracy of quantitative analysis will be inferior to that of electron probe microanalysis.

In spite of these disadvantages, we anticipate that the potential of this instrument in microanalysis is enormous. The possibility of applying this type of trace analysis on the micron dimensional level to biological specimens is particularly intriguing. The usefulness and importance of the technique to the study of mineralogical specimens has already been demonstrated [7]. We expect to be active before

the end of the fiscal year '72 in the study of both the instrument and its applications.

Adding the Ion Microprobe Mass Analyzer will require some reorganization of the available laboratory space. Studies of plans for this reorganization are presently under way.

The Division-wide computerized data acquisition system has been mentioned previously [6]. Midway through this fiscal year, the computer was delivered and put into operation by the Technical Services Group of the Division. They have prepared and installed part of the interfacing equipment which will be needed to join various experiments to the system. None of our equipment is on-line yet, but we are planning to use the system with the following devices: electron probe microanalyzer, x-ray fluorescence spectrometer, three optical emission spectrometers and a microphotometer. In each of these applications we will begin with simple data collection. (Each instrument is currently capable of transferring digital data to a teletype.) In addition, the interfacing for the electron probe will include, at an early stage, control provisions for beam positioning. Other extensions will be made on an add-as-we-go basis.

Preliminary programming for the Division computer has been carried out by Robert Myklebust. He has adapted MULTI 8 (see Section 4.C) for processing electron probe data on the new computer. Other programming and computer usage has continued with the NBS Univac 1108 and with a variety of time-sharing services.

B. Personnel and Activities

A list of the present personnel of the Section is given in Section 6. Aside from the changes in Summer Assistants, the following changes should be noted. B. F. Scribner, Section Chief, was promoted in January of 1971 to Deputy Division Chief of the Analytical Chemistry Division. The

administrative tasks of Section 310.02 were transferred to K. F. J. Heinrich (now Acting Section Chief), with assistance by S. D. Rasberry (now Acting Assistant Section Chief). V. C. Stewart and D. M. Bouchette retired, and J. R. Hénoc (Guest Worker), B. L. Hammond (Research Associate), E. Belkas (Guest Worker), B. W. Pastine (Chemist, part-time), and C. P. Wren (part-time clerical) ended their activities within the Section.

The Section has endeavored to maintain the research and service activities on a satisfactory level, in face of this drastic reduction in force. As previously, the personnel are grouped into four task forces: 1. Optical Emission Spectroscopy, 2. X-ray Fluorescence Spectrometry, 3. Electron-Probe Microanalysis, and 4. Enrichment Techniques. Within each of these task forces, the activities continue being divided between (a) research and development, and (b) service activities.

In optical emission spectroscopy, the position of research spectroscopist has been vacant; our research effort was mainly concentrated on the characterization of materials of interest in pollution studies, such as the analysis of river bottom sediments, and proposed Standard Reference Materials. We have now secured an investigator who will re-initiate research into the more theoretical aspects of optical emission spectroscopy, particularly the potentials of novel and unconventional excitation sources. These activities will commence in the fall of 1971.

As in previous years, a large number of determinations were performed by x-ray fluorescence spectrometry on proposed Standard Reference Materials, as well as on other types of specimens. Analytical research in this area resulted in novel and greatly improved calculation procedures for the correction of interelement effects in complex matrices.

In electron probe microanalysis, we have continued the projects on which we were working the previous year.

The computer program COR has been cast into a definite form and is now considered completely debugged; the extensive work of documentation which is necessary to make this procedure effectively available to other research analysts is almost completed, and a Technical Note containing the program and its documentation will be forthcoming soon. The program, as well as the shorter correction program MULTI 8, was used in the interpretation of further experimental measurements on the microprobe Standard Reference Materials in the gold-silver and gold-copper systems [8]. The results of these measurements were documented and discussed in an NBS Special Publication [9] issued in summer of 1971.

We have started an investigation of the analysis of particles and thin films, particularly biological thin sections. This year, we were concerned mainly with scanning transmission techniques, and with mounting media for such specimens. The aspects of x-ray detection and quantitative evaluation will be considered in detail at a later time.

Our research in preconcentration techniques, in combination with spark source mass spectrometry, has produced a method for the determination of mercury, and other elements, in biological materials. These techniques are a prerequisite for characterizing Standard Reference Materials of this type.

Due to lack of personnel, the activities in bibliographic areas were restricted to keeping up our awareness files, particularly in electron probe microanalysis.

The research activities outlined above, as well as analytical service performed, will be discussed in more detail in the ensuing chapters.

K. F. J. Heinrich and S. D. Rasberry

2. OPTICAL SPECTROSCOPY

A. Research

During the past year, few resources could be allocated to excitation studies. In consequence, we have worked mainly on improving spectrochemical methods of analysis and have studied the limitations of these methods relative to the Standard Reference Materials (SRM's) for which we are responsible. This work is documented more fully in sections B and C of this chapter.

Major improvements in spectrochemical analysis seem to be imminent, especially in the area of excitation sources; consequently, we are anxious to pursue this field. We have been successful in recruiting an active investigator who is interested in this specific area. Dr. Danold Golightly will join our staff in September 1971 to conduct basic and applied research into excitation sources for spectrochemical analysis.

B. Applications to Analysis

The optical emission instrumentation at our laboratory is employed for analytical work as well as for research activities. For the period July 1970 through June 1971, analyses were performed by optical emission spectroscopy involving 318 samples, 9569 determinations, and 97 reports. Some high points of the analyses will be described.

1. Analyses of Standard Reference Materials

As in the past, optical emission spectroscopy has continued to perform an important role in the program for production and certification of SRM's. The ultimate output of this activity is the issuance of well-characterized SRM's certified for their chemical composition. Studies are performed in cooperation with the Office of Standard Reference

Materials, with other Sections of the Analytical Chemistry Division, and with various laboratories in industry, universities, and Government.

The contribution of the optical emission group to this program consists of four phases: (1) preliminary analysis for acceptance, (2) study of homogeneity of the bulk material, (3) quantitative analyses of the material, and (4) measurements on Standard Reference Materials to test their utility with given methods of analysis.

Analysis for acceptance for some materials often involves only a semiquantitative method employing dc-arc excitation. This screening process will show if the material is pure enough for the intended purpose. For other materials such as alloys, analysis usually involves highly precise and accurate methods to ensure compliance with composition requirements.

Once the material has been accepted as having the desired composition, the next step is to test the homogeneity to ensure suitability for the intended use. A common procedure is to select samples from chosen positions in the bulk material and to analyze these samples for the important elements. In this work, emphasis is placed on precision rather than accuracy since, at this time, we are interested in differences among samples rather than absolute determination of composition. Experiments have been designed to obtain the maximum information from the minimum measurements, but employing both optical emission and x-ray fluorescence spectrometers to increase the power for detection of inhomogeneity. A more complete description of this testing is given in Section 2.C of this report.

Next, we are involved, although to a lesser degree, in the analyses for certification of Standard Reference Materials. Here the spectrochemical analysis must be made by a

primary method relative to standards synthesized from pure materials. The samples are converted to powders or to solutions to provide a form for comparison with the synthesized standards. Powders are usually analyzed by controlled arc excitation, and solutions by the plasma jet or by the spark and rotating electrode technique.

The final step in our contribution to Standard Reference Material production is the intercomparison of those Standard Reference Materials used in emission spectroscopy to test their workability with currently used methods of spectrochemical analysis. It is recognized that differences in structure and/or combinations of elements in given classes of Standard Reference Materials may change signal intensities. Hence, the history of preparation of materials, and the presence or absence of tramp elements may result in Standard Reference Materials that yield calibration curves which are displaced. Such displacements frequently can be minimized or eliminated by changing the excitation conditions; however, this information is vital to eventual users.

Compatibility studies also are made to ensure standardization of the measurement system. Further, work is undertaken to optimize discharge conditions for particular alloy systems. During the past year, we have made many determinations on the 1261-1265 set of low-alloy steels to test the compatibility of these Standard Reference Materials with existing methods. A publication of this work is forthcoming.

Examples of certificates for Standard Reference Materials issued in the past year, to which this Section contributed, are given in the Appendix.

2. Other Service Analyses

This Section performs many analyses for groups within NBS and for other Government Agencies. Most analyses are surveys by optical spectroscopy in which 50 to 70 elements

are sought. This type of analysis is semiquantitative and quite often provides sufficient information for the solution of a problem. A wide variety of samples were examined in the past year by this method. Sample size ranged from micro-size particles to large sections of metal from which appropriate samples were taken. The typical sample was one ranging from 5- to 20-mg total weight. For those samples weighing less than 0.5 mg, the identification of major metallic constituents was often the only data required. For the other samples, 50 to 70 elements were determined semiquantitatively or reported as not detected. Typical analyses include air pollution samples, sediments from natural waters, enzymes, cloth, vegetation, detergents and cleaning compounds, surface scale, and thin-film deposits on glass.

Quantitative analyses are frequently performed to determine if a part of a machine or structure is the alloy specified by the designer. These analyses are usually part of a detailed failure study made at NBS. An example of this is the investigation of the cause of an aircraft wing member failure which led to its crashing. In this case, the chemical composition was correct for the alloy specification; it was learned later that improper heat treatment was responsible for the failure. Another example is the analyses of aluminum plate and weld joints of a liquid oxygen tank car which exploded, causing several deaths. Material of the tank car was scattered over a large area, and by determining the composition of aluminum alloy fragments collected at several locations, the direction of the blast, and ultimately its cause, was determined.

We are also called on to perform analyses of materials in failure avoidance programs. For example, a number of nuts, bolts, washers, and concrete studs and anchors have been submitted in the past year by the District of Columbia Department of Highways and Traffic for alloy identification.

This material is for use in the subway system now being built in Washington, D. C. Because of the possibility of corrosion, the parts are specified to be type 304 stainless steel. However, our analyses showed that a large fraction of the submitted material was not 304 stainless. Consequently, several lots had to be rejected (Figure 1).

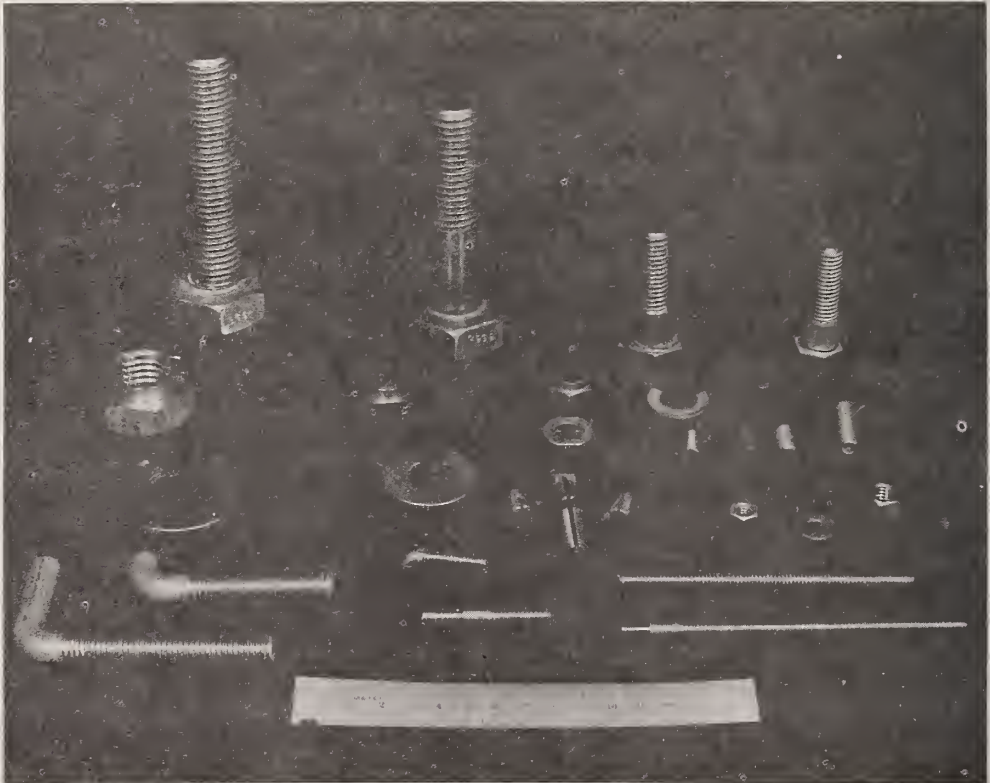


Figure 1. Hardware analyzed for alloy identification, for the District of Columbia Department of Highways and Traffic for alloy identification.

C. Description of Homogeneity Testing Method

In the last publication of this series [6], the homogeneity testing of materials intended as spectrochemical Standard Reference Materials was described. This year we will describe the homogeneity testing procedure for Standard Reference Materials which are machined into chips primarily for use in checking chemical methods of analysis. An illustration of a typical sampling procedure for homogeneity testing is shown in Figure 2.

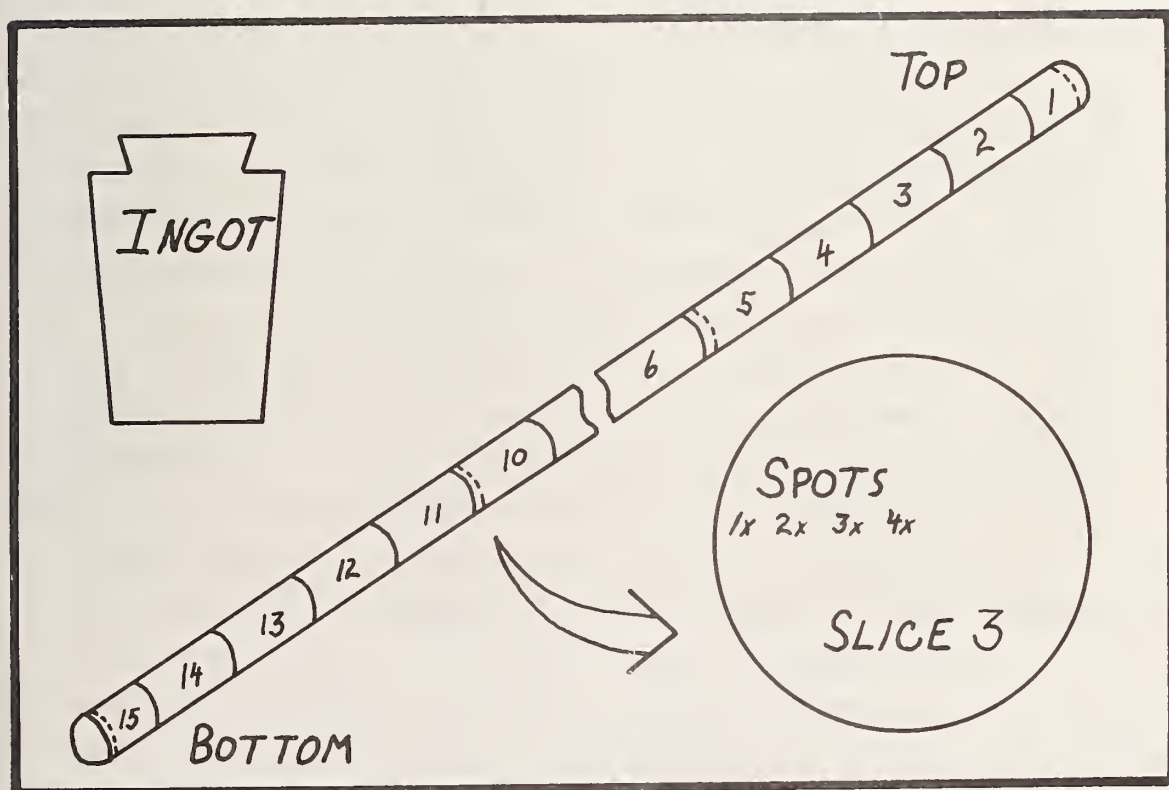


Figure 2. Sampling of steel bar for homogeneity studies.

Typically, an ingot is cropped, forged, and rolled up into a round bar $5 \frac{1}{4}$ inch in diameter. This bar is cut into approximately 36-inch (92-cm) sections with care being taken to preserve identity of each section's relative position. Based on the results of homogeneity testing, sections are selected for machining on lathes with special tools to provide metal chips of a uniform and desired size and to the requisite homogeneity. The chipping process stops when the sections are reduced typically to a diameter of $1 \frac{3}{4}$ inches (4.4 cm) because of physical and economic considerations. Chipping may be stopped at any diameter shown by the testing to be the beginning of excessive inhomogeneity. The choice of test positions on the cross sections also makes it possible, should suitable homogeneity be observed, to further process the cores remaining after chipping to the usual solid disk samples for use in optical emission and x-ray spectrometric methods of analysis. For most materials, however, the required homogeneity for spectrometric analysis can be achieved only by special melting, casting, and fabrication procedures.

In the illustration, slices, about $\frac{3}{4}$ -inch (1.9 cm) thick, are taken from the front-face of section 1 and tails of sections 5, 10, and 15 to provide samples to determine if variations in chemical composition occur along the length of the bar. Similarly, each of the slices is samples at four positions (spots) along the cross-section to determine if radial inhomogeneity occurs. The positions of these spots are at radii of zero (center), $\frac{7}{8}$ -inch (2.2 cm) (where chipping typically stops), $1 \frac{11}{16}$ -inch (4.3 cm) (mid-point of chipping), and $2 \frac{1}{2}$ -inch (6.4 cm) (where chipping starts). A cross-section of one of the slices is shown in the lower right corner of Figure 2 with the spots for sampling indicated. The sixteen positions thus chosen are representative of the extremes of the bar.

The instrumental methods employed in the homogeneity testing, usually optical emission or x-ray fluorescence spectrometry, are subject to linear trends with time (drift). Therefore, the measurements are run in a sequence which is designed to balance the effects of these trends. The experimental design was devised by NBS statisticians for our needs [10]. The time-sequence of individual measurements is arranged in such a way that linear drift does not introduce a false concentration gradient, either longitudinally or radially. To determine a time-sequence design, we establish a matrix in which each row represents one slice and each column represents the distance of a spot from the center. We then assign to each location in this matrix a number indicating the order measurements are to be made. The numbers are chosen so that the sums for all rows are equal and the sums for all columns are equal. This distributes the effects of drift evenly over all the rows and columns. An illustration of this is shown in Figure 3. The first measurement to be made is that of position (1,1) of the matrix; i.e., slice 1, spot 1. Next follows position (2,3), slice 2, spot 3. The sixteenth measurement is made at slice 3, spot 3. This sequence usually is repeated at least four times to provide adequate data for suitable statistical evaluation.

Data from the emission and x-ray spectrometers are recorded directly in digital form and entered into a computer for analysis of variance. A computer output sheet for a four-slice by three-spot array (center spot not used in this case) is shown in Figure 4. The material used for this illustration is cast iron and the element to be tested for homogeneity is phosphorus. While the material is to be certified for phosphorus to the third decimal place only, the computer calculates a value to the fifth decimal place. The last two decimal places provide important information regarding the variation in the third decimal place. In the example given, no excessive inhomogeneity was observed for phosphorus.

		SPOT				
		1	2	3	4	
SLICE	1	1	12	7	14	34
	2	8	13	2	11	34
	3	10	3	16	5	34
	4	15	6	9	4	34
		34	34	34	34	

RUN NO.	1	2	3	4	5	--	13	14	15	16
SLICE	1	2	3	4	3	---	2	1	4	3
SPOT	1	3	2	4	4	---	2	4	1	3

Figure 3. Time-sequence of measurements for a four-slice by four-spot homogeneity test.

D. Modification of Gas-Sheath Arc Unit

Various types of gas-sheath arc units -- developed both at NBS and elsewhere -- which exclude atmospheric oxygen and nitrogen from the vicinity of the arc have been in use in this laboratory for a number of years. An improved gas-sheath arc unit which we developed to overcome a number of problems encountered in using the other units has now been in use on all dc-arc runs for a period of six months. This unit is

HOMOGENEITY OF 20G. QVAC ANALYST-JL WERER 11/26/71
 ELEMENT P
 ANALYSIS OF VARIANCE

	DF	SUM OF SQUARES	MEAN SQUARE	F
TOTAL	47	2.14414-05	4.56201-07	1.73
TREND	4	1.56560-06	3.91401-07	1.48
RUNS	3	7.74385-06	2.58128-06	9.77
SLICE	3	2.75009-06	9.16698-07	3.47
SPOT	2	1.31192-07	6.55960-08	.25
ERROR	35	9.25068-06	2.64305-07	

SD .00051
 AVG .01300
 CV 3.95466
 TL .00026
 CF .0000920

AVERAGES

	SPOT 1	SPOT 2	SPOT 3	AVG.
SLICE 1	.01297	.01308	.01347	.01317
SLICE 2	.01313	.01338	.01338	.01330
SLICE 3	.01251	.01269	.01299	.01273
SLICE 4	.01313	.01290	.01239	.01280
AVERAGE	.01293	.01301	.01306	.01300

Figure 4. Computer output for analysis of variance of the phosphorus concentration in cast iron

a modification of a commercially available unit which is easy to disassemble and clean between individual runs. The major problems which have been encountered were related to electrode positioning and cooling, control of the atmosphere around the arc to give satisfactory burns, and removal of dense fumes when samples of up to 100 mg were run. These problems have been solved in the design shown in Figure 5. A detailed drawing with exact dimensions will be included in a later publication.

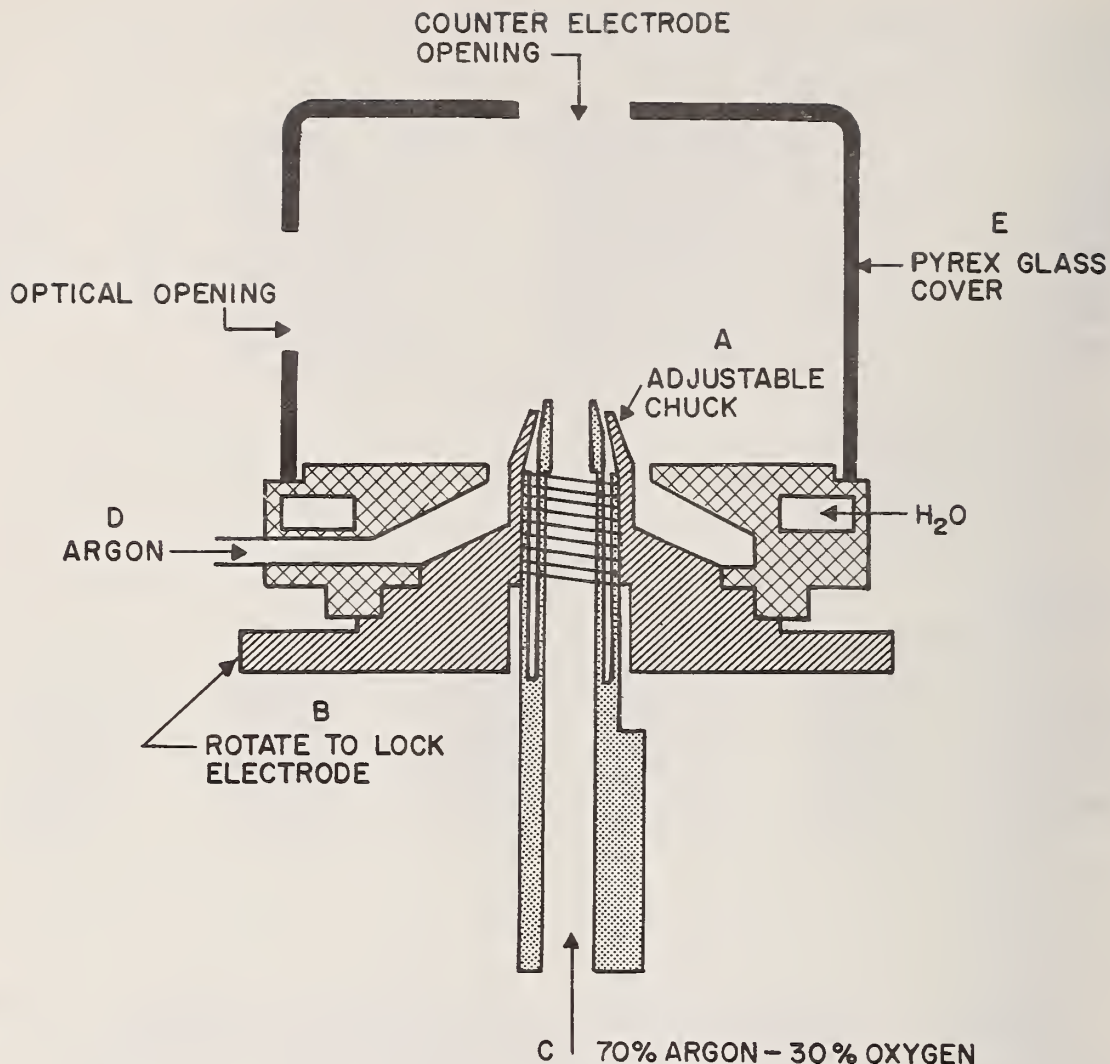


Figure 5. Schematic drawing of the modified gas-sheath arc unit.

In the modified version, the sample electrode is held in an adjustable chuck (A) in such a manner that the exact electrode height above the base can be adjusted easily and locked in position by rotating the base extension (B). This arrangement gives improved water cooling and excellent electrical contact without danger of arcing around the electrode. It also eliminates freezing of electrodes in the holder,

even on long-time, high amperage runs. The jaws of the chuck have been designed to allow a flow of gas -- 70% argon + 30% oxygen -- which enters at the bottom of the chuck (C) to form an envelope around the electrodes. A stream of 100% argon, which enters at D, flows through an enlarged opening around the chuck filling the chamber formed by the cover (E) with argon. This excludes air which might be pulled into the chamber at the opening for the optical path. Breakage of the chamber cover has been reduced by replacing the small quartz dome with a larger-volume pyrex cover. This also allows better dilution and removal of dense vapors formed with samples such as lead oxide. The flow rates of the two gas lines (100% A and 70% A + 30% O₂) can now be adjusted independently to suit the requirements of the particular samples being run.

J. L. Weber, M. M. Darr

3. X-RAY FLUORESCENCE SPECTROMETRY

As in past years, the x-ray fluorescence spectrometry laboratory has served a dual role in performing both research and service. The broad aim of our research has been to seek improvements in methodology which will increase the accuracy of this technique or widen its applicability. In some cases where we were consulted, lowering a detection limit or increasing the speed of analysis has been critical to extending x-ray fluorescence to a new application. In other instances, communication has been the barrier and our role has been to show others how existing x-ray methodology can be applied to new problem areas.

A. Instrumentation

Our instrumentation for x-ray fluorescence has been reviewed in prior technical notes of this series [1-6]. In the latter reference, details are given of the improvements made on our single-channel vacuum x-ray fluorescence spectrometer. This instrument has continued to be our main tool in both research and applied work.

The only change made to the single-channel x-ray spectrometer over the past year is the addition of a removable gas fitting for the purpose of introducing helium into the spectrometer housing. The need for a helium filling to reduce x-ray absorption arises occasionally; for example, in determining light elements (from magnesium to calcium) in volatile liquids. In such cases, evacuation of the spectrometer is not practical, especially when disposable, non-hermetic liquid holders are to be used. In our modified instrument, helium is continually leaked into the spectrometer through a fitting attached to the vent port; this maintains a positive pressure of helium. Each time samples are introduced into the device,

the mechanical vacuum pump is operated for about three seconds to expel the air which is introduced.

The use of lithium-drifted silicon solid state detectors has been demonstrated by the electron-probe group [6] to considerably increase their efficiency in performing qualitative analyses. Further, reports in the literature [22] indicate the usefulness of these detectors for quantitative analysis at trace levels. These were two of several factors which led us to purchase a large-area (80 mm^2) lithium-drifted silicon detector. It was received in the last week of the fiscal year; consequently, the details of even its earliest applications will be given in next year's report. Performance tests of the detector indicate unusually good energy resolution for a large-area detector (see Figure 6). At low count rates,

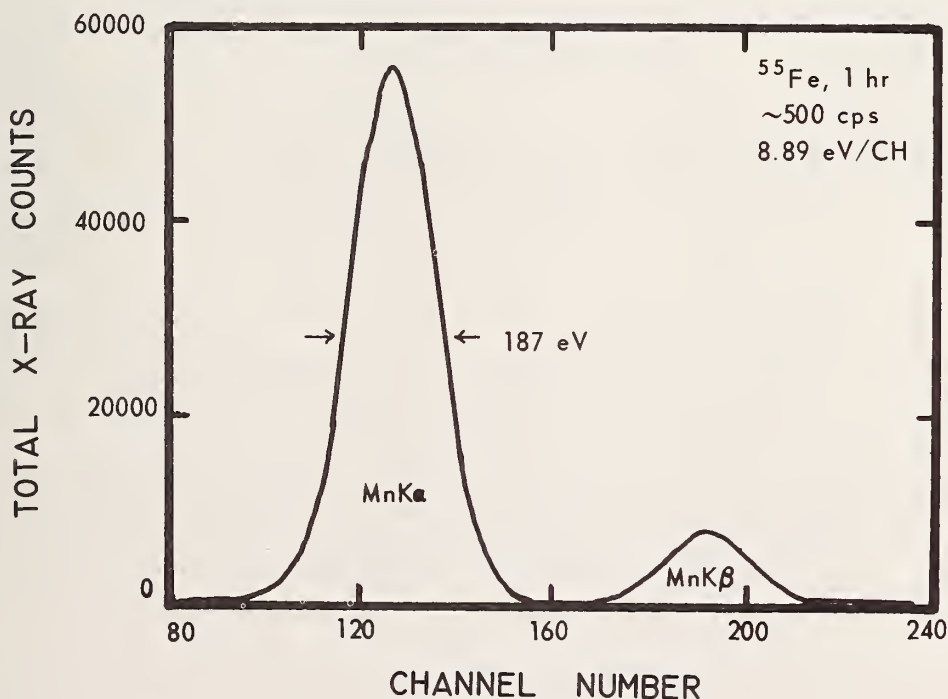


Figure 6. Resolution test for our lithium-drifted silicon detector. A spectrum obtained by directly counting x-ray emission from an iron-55 radioisotope.

resolution for MnK α x-rays was found to be less than 190 eV width at 50% of peak height (FWHM). At higher total count rates (up to 20,000 cps), the resolution degrades by only about 20 eV.

B. Computations for Quantitative Analysis

A substantial part of our research effort this year has been a continued study of empirical calibration techniques for quantitative x-ray fluorescence analysis in the presence of interelement effects [12-14]. An account of this study, together with a detailed discussion of the computation procedure we have developed, will be presented to the Colloquium Spectroscopicum Internationale XVI in October, 1971. An extended abstract of the work will be published at that time. Here we wish to indicate the nature of the problem and some of the results we have obtained with a new computation procedure

Characteristic x-rays emitted by an element in a matrix emerge only after undergoing partial absorption, the extent of which is dependent upon what elements are present in the matrix. If we neglect the effects of differences in primary radiation, and the mass absorption coefficients are nearly the same for the measured element and the matrix, the relative intensity is directly proportional to the concentration of the element. This is illustrated by case A in Figure 7. In case B, the absorption by the matrix is greater than that of the element; consequently, the measured intensity is depressed. We have confirmed, experimentally, that in this case binaries follow a hyperbolic function:

$$R = \frac{C}{C + \alpha(1-C)} , \quad (1)$$

where R is the measured relative intensity (assumed corrected for background and counting deadtime), C is the concentration of the measured element (mass fraction), and α is a constant.

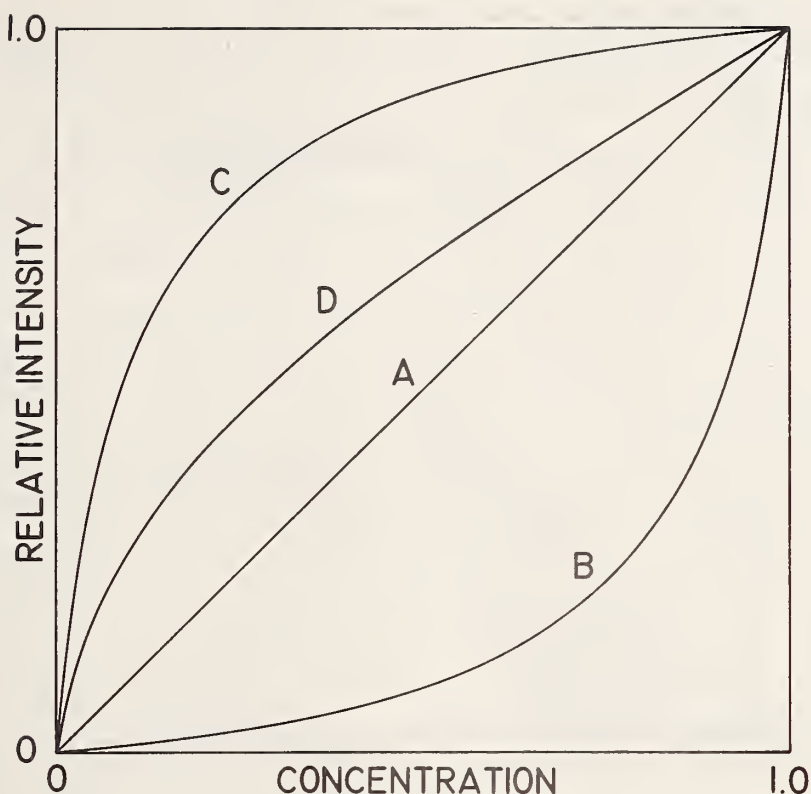


Figure 7. A qualitative representation of possible interelement effects; A. No interelement effect, B. Absorption, C. Transparency of matrix, D. Secondary fluorescence.

The magnitude of α depends upon the displacement of the hyperbola from the degenerate, straight-line case. The value of α must be a positive, real number; it is greater than one for absorption, where the measured intensity is depressed. When the specimen absorbs the radiation less than does the pure element used as a standard, "negative" absorption (transparency of matrix) results. See case C. Other workers [14] imply that this curve also is fit by the hyperbolic equation (α is less than one). A fourth case, secondary fluorescence, is sometimes obtained and is illustrated in Figure 7 as case D. Secondary fluorescence occurs in conjunction with the photoelectric absorption by the analyte element of a characteristic x-ray produced by one of the matrix elements. We have

confirmed, by experiment, the fact that this case does not follow exactly a hyperbolic function. This is intuitively reasonable since fluorescence must increase with the concentrations of both the exciting and the excited element. When the concentration of the analyte is near unity, there is very little of the exciting element available to cause secondary fluorescence; however, in a binary, at the lower concentrations of the analyte, an increase in the effect is noted due to the greater presence of exciting element.

Calibration data of the type illustrated in Figure 7 can be studied more incisively if C/R is plotted as a function of C , as is illustrated in Figure 8. When this is done, the horizontal line, $C/R = 1$ for all C , denotes the case of no net effect of either absorption or fluorescence. Points where absorption is dominant have C/R values greater than unity due to the reduction in relative intensity and consequently fall above the "no effect" line. Conversely, when secondary fluorescence is dominant, the points fall below the "no effect" line.

An important feature of the graph of C/R as a function of C is the fact that the hyperbolas plotted in Figure 7 are represented as straight lines with this new choice of coordinates. The experimental data presented in Figure 8 are for the calibration of iron in alloys containing iron, nickel and chromium; the upper boundary curve represents the case of Fe absorbed by Cr in Fe-Cr binaries, whereas the lower curve shows the secondary fluorescence of Fe by Ni in Fe-Ni binaries. All intermediate points (closed circles) are for Fe in Fe-Ni-Cr ternaries.

In order to establish a calibration equation which will permit the determination of Fe in the presence of Ni and Cr, we make two observations regarding Figure 8. First, whatever equation is selected must be appropriate in the absence of either Ni or Cr, i.e., it must fit the boundary conditions of both binary curves. Secondly, it must take into account

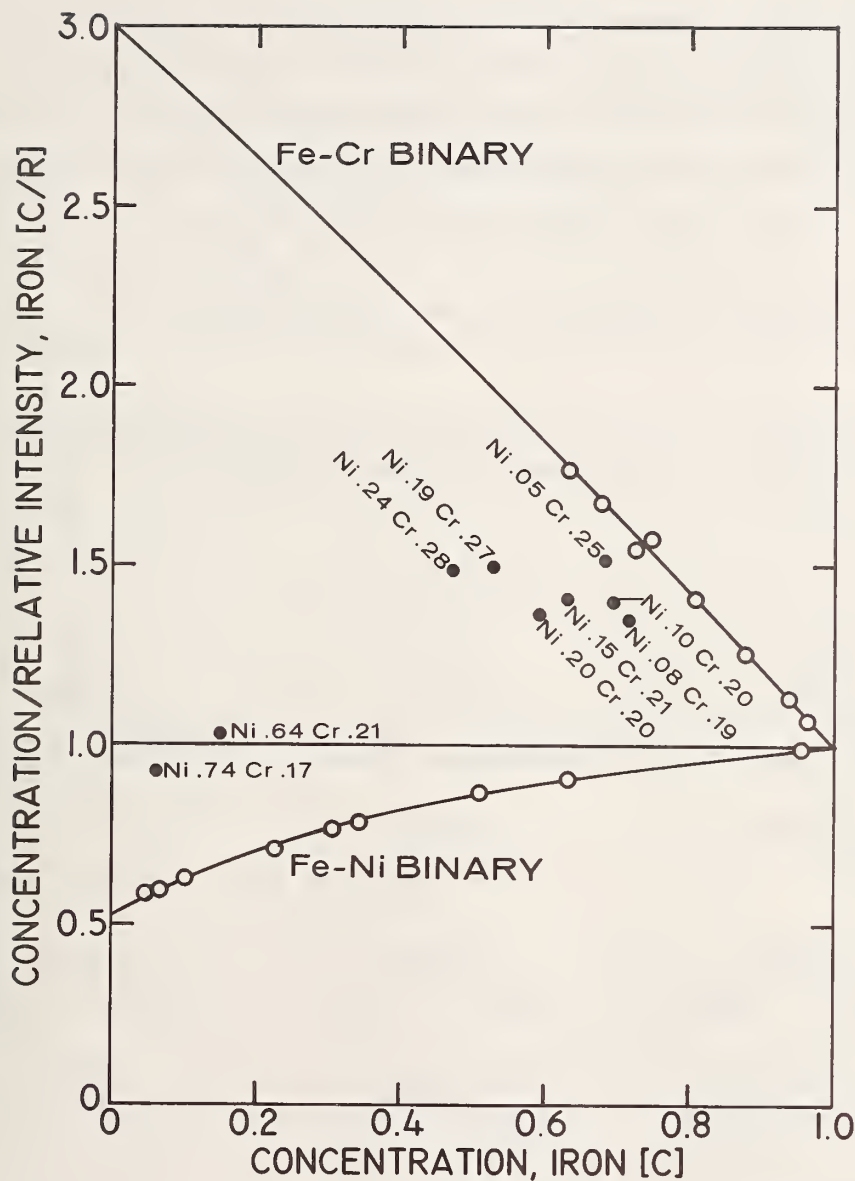


Figure 8. Experimental data for the determination of iron in ternary alloys of iron, chromium and nickel.

the non-hyperbolic curvature observed in the case of secondary fluorescence. We make the assumptions in this study that the x-ray intensities are obtained from specimens which are infinitely thick to x-ray penetration, are homogeneous, and have smooth surfaces.

We have measured x-ray intensities for a set of standards and unknown Fe-Ni-Cr alloys. These data have been submitted to the new computation procedure mentioned above and also to a procedure which treats secondary fluorescence as "negative" absorption. The results are summarized in Table 1. In this table the new procedure is abbreviated "PBM2", while the "negative" absorption procedure is abbreviated "N-A".

Table 1. Results (in mass fraction) for Fe-Ni-Cr alloys using two computation procedures*

<u>Specimen</u>	<u>Element</u>					
	<u>Fe</u>		<u>Ni</u>		<u>Cr</u>	
	<u>Given</u>		<u>Given</u>		<u>Given</u>	
	<u>PBM2</u>	<u>N-A</u>	<u>PBM2</u>	<u>N-A</u>	<u>PBM2</u>	<u>N-A</u>
<u>5054</u>	<u>0.7250</u>		<u>0.0015</u>		<u>0.2577</u>	
	.7257	.6779	.0016	.0016	.2497	.2740
<u>5202</u>	<u>.6303</u>		<u>.1480</u>		<u>.2130</u>	
	.6300	.589	.1511	.159	.2067	.242
<u>5364</u>	<u>.4721</u>		<u>.2357</u>		<u>.2784</u>	
	.4776	.471	.2413	.246	.2650	.270
<u>3987</u>	<u>.3431</u>		<u>.6552</u>		<u>.0000</u>	
	.3403	.171	.6540	.827	.0000	.0001
<u>1188</u>	<u>.0616</u>		<u>.7370</u>		<u>.1540</u>	
	.0663	.0639	.7227	.752	.1405	.140

*The values underlined are given by wet chemical analysis. PBM2 is the new procedure and N-A is the "negative" absorption procedure.

The results by the new procedure agree reasonably well with the wet chemical values, generally within 2% to 4%, relative. There appears to be no degradation in accuracy in cases of severe secondary fluorescence, where the "negative" absorption method may be prone to failure. See, for example, Fe in specimen 3987.

C. Characterization of Standard Reference Materials

Approximately 1500 man-hours have been spent this year in performing 7500 separate quantitative determinations by x-ray fluorescence methods. Some of these determinations have been for service analysis; however, most of them have been undertaken in the characterization of Standard Reference Materials.

We are routinely called on to support the production of Standard Reference Materials in five distinct ways. These are cited below, with an example drawn from this year's work to illustrate each one.

1. Preliminary Testing

When a material is received at NBS proposed as a Standard Reference Material, it is usually subjected to a preliminary test of composition by rapid instrumental methods. Preliminary tests of this kind, together with the examination of physical characteristics, formed the basis for rejection of the first lot of Special Steel 1264 produced. X-ray fluorescence was a help in making the decision to reject the lot and to begin production of a new lot. The second lot of 1264 passed preliminary testing and, as have the other four Standard Reference Materials in the set of Special Steels 1261-1265, exhibited suitable homogeneity by x-ray fluorescence methods. To date, all five have been certified for the important specified elements and additional certification is underway. Certificates for these standards are appended to this report.

HOMOGENEITY TEST - UNIVERSAL
ELEMENT CA
ANALYSIS OF VARIANCE

-- 6-71

	DF	SUM OF SQUARES	MEAN SQUARE	F
TOTAL	127	4.38028+00	3.44904-02	2.25
TREND	4	4.14672-01	1.03668-01	6.75
RUNS	3	2.16845+00	7.22817-01	47.08
SLICE	15	1.78033-01	1.18639-02	.77
SPOT	1	2.23257-02	2.23257-02	1.45
ERROR	104	1.59630+00	1.53538-02	

SD .12391
AVG 63.20000
CV .19606
TL .06196
CF .0002700

AVERAGES

	SPOT 1	SPOT 2	AVG.
SLICE 1	63.20	63.21	63.21
SLICE 2	63.16	63.22	63.19
SLICE 3	63.19	63.29	63.24
SLICE 4	63.29	63.13	63.21
SLICE 5	63.21	63.29	63.25
SLICE 6	63.13	63.18	63.15
SLICE 7	63.18	63.14	63.16
SLICE 8	63.12	63.20	63.16
SLICE 9	63.22	63.22	63.22
SLICE10	63.22	63.23	63.22
SLICE11	63.09	63.23	63.16
SLICE12	63.15	63.12	63.13
SLICE13	63.25	63.22	63.24
SLICE14	63.23	63.17	63.20
SLICE15	63.21	63.33	63.27
SLICE16	63.13	63.25	63.19
AVERAGE	63.19	63.21	63.20

Figure 9. Homogeneity test for calcium in Portland Cement. Analysis of variance data are presented, followed by the value obtained for calcium concentration at individual test locations.

2. Homogeneity Testing

The next phase of Standard Reference Material production is perhaps the most important of all. The function of homogeneity testing is to determine how uniform, in terms of composition, is the material to be sold. Some discussion of the experimental designs we use in measuring homogeneity is given

in a previous note in this series [6] and in Section 4.C of this report. Besides the work mentioned above for steels, we have also determined the homogeneity for seven new Portland Cement Standard Reference Materials. In Figure 9 and 10, complete results are shown for one of the materials. A summary for all the materials is given in Table 2.

HOMOGENEITY TEST - UNIVERSAL
ELEMENT S
ANALYSIS OF VARIANCE

-- 6-71

	DF	SUM OF SQUARES	MEAN SQUARE	F
TOTAL	127	3.19778-02	2.51794-04	1.58
TREND	4	7.52766-04	1.88191-04	1.18
RUNS	3	4.38183-03	1.46061-03	9.19
SLICE	15	1.02739-02	6.84925-04	4.31
SPOT	1	3.34153-05	3.34153-05	.21
ERROR	104	1.65359-02	1.58999-04	
SD	.01261			
AVG	2.20000			
CV	.57316			
TL	.00630			
CF	.0000400			
AVERAGES				
	SPOT 1	SPOT 2	AVG.	
SLICE 1	2.180	2.183	2.182	
SLICE 2	2.200	2.194	2.197	
SLICE 3	2.181	2.189	2.185	
SLICE 4	2.200	2.192	2.196	
SLICE 5	2.193	2.196	2.195	
SLICE 6	2.180	2.199	2.190	
SLICE 7	2.203	2.211	2.207	
SLICE 8	2.204	2.220	2.212	
SLICE 9	2.195	2.201	2.198	
SLICE10	2.212	2.191	2.202	
SLICE11	2.191	2.227	2.209	
SLICE12	2.227	2.193	2.210	
SLICE13	2.213	2.206	2.209	
SLICE14	2.204	2.195	2.200	
SLICE15	2.215	2.205	2.210	
SLICE16	2.194	2.204	2.199	
AVERAGE	2.199	2.201	2.200	

Figure 10. Homogeneity test for sulfur (calculated as SO_3) in Portland Cement. Analysis of variance data are presented, followed by the value obtained for sulfur concentrations at individual test locations.

Table 2. Summary of results for x-ray fluorescence tests
of homogeneity on seven new Portland Cement
Standard Reference Materials

<u>SRM Number</u>	<u>Nominal Concentration (in wt. %)</u>		<u>Standard Deviation (in wt. %)</u>	
	<u>Ca</u>	<u>SO₃</u>	<u>Ca</u>	<u>SO₃</u>
633	65	2.2	0.14	0.013
634	63	2.2	.13	0.013
635	60	6.8	.14	0.028
636	64	2.2	.15	0.015
637	66	2.4	.14	0.013
638	62	2.4	.11	0.014
639	67	2.5	.08	0.018

3. Certification of Composition

Certification of composition is not normally undertaken by methods of analysis which rely on standardization by reference materials of similar type, except in the case of replacement for a Standard Reference Material going out of stock. In these cases, a precise relative method, such as x-ray fluorescence, can be very useful in determining the composition values to be certified. This year, a titanium alloy (6Al-4V) was certified using x-ray fluorescence as a principal measurement technique. The certificate for this material is appended.

4. Utility of Standard Reference Materials

When a Standard Reference Material is issued as a calibration standard for an instrumental method of analysis and has been certified by umpire wet chemical procedures, it is necessary to test directly the utility of the material

to the method for which it is intended. Tests of this type were undertaken this year on two Standard Reference Materials which are important to air pollution control. Two new sulfur-bearing oil Standard Reference Materials were produced in order to extend downward the range of concentration of sulfur in oil offered by the NBS. This extension has become important in view of tighter sulfur-emission controls incorporated into the pollution laws of many cities. The new Standard Reference Materials were found to be consistent with the two previous ones, when all four are measured according to ASTM Standard Method D 2622-67 for x-ray fluorescence determination of sulfur in oil. A graph of the calibration curve obtained is presented in Figure 11. Certificates are appended.

5. Production Quality Control

In some cases, Standard Reference Materials of quite different compositions are identical in appearance and can therefore be mislabeled accidentally. We use x-ray fluorescence to check the identity and labeling of such Standard Reference Materials because the technique is not destructive and does not alter the condition of a specimen which may be ready for sale. In one instance this year, ten specimens, labeled 1172, were suspected of being incorrectly labeled. They were submitted to us and on the same day a report was issued verifying the ten specimens as Standard Reference Material 1172. Accurate determinations of niobium and chromium for each sample confirmed the identities with less than one man-hour required to perform the task.

D. Service Analyses

The service analyses we perform are undertaken in support of NBS projects as well as to aid important work underway at other Government Agencies. Typical analyses include:

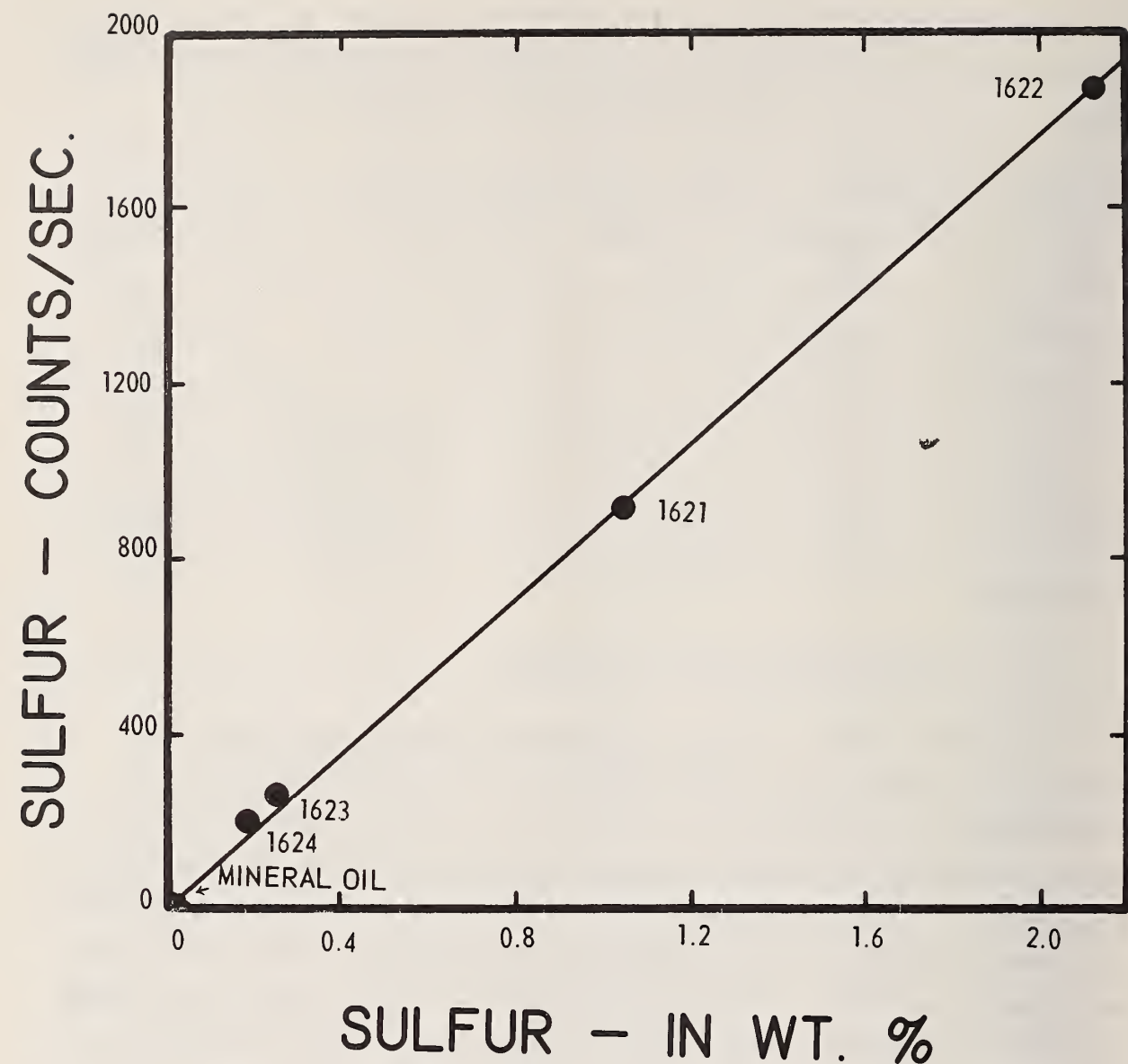


Figure 11. X-ray fluorescence calibration curve for the determination of sulfur in oil. The analytical procedure used follows ASTM Standard Method D 2622-67.

1. Stainless steel for fabrication of parts for the NBS nuclear reactor. Stringent composition specifications must be met in this application for both mechanical safety and radiation safety reasons.

2. Fasteners and components to be used in the subway system which is being constructed in metropolitan Washington, D. C. Safe operation and economical future maintenance of this system depend on both proper design and use of the specified materials.

3. Iron foils for a research project being carried out at NBS were analyzed. The role minor elements were playing in the requester's experiments was being studied.

E. Investigation for Special Applications

Cooperation and consultation with the NBS group responsible for research in fabric flammability has introduced to us a problem to which an x-ray fluorescence technique may provide a solution.

Phosphorus compounds have been proven as flame retardants when "set" in textiles. Numerous methods exist for determining phosphorus in cloth when the cloth can be sampled. However, a rapid non-destructive technique, which can be used on-line in the treating area of a mill, is needed for quality control of the phosphorus concentration. We have demonstrated (see Figure 12) that tube-excited x-ray fluorescence meets some of the requirements for this kind of quality control. Furthermore, we discussed the problem with the AEC group for development of radioisotope applications and they have arranged for demonstrations of the feasibility of using isotope-excited x-ray fluorescence in this application.

Not all the problems connected with the determination of phosphorus in cloth have been solved in the brief study which has been thus far undertaken. We hope to present more detailed results in a later report.

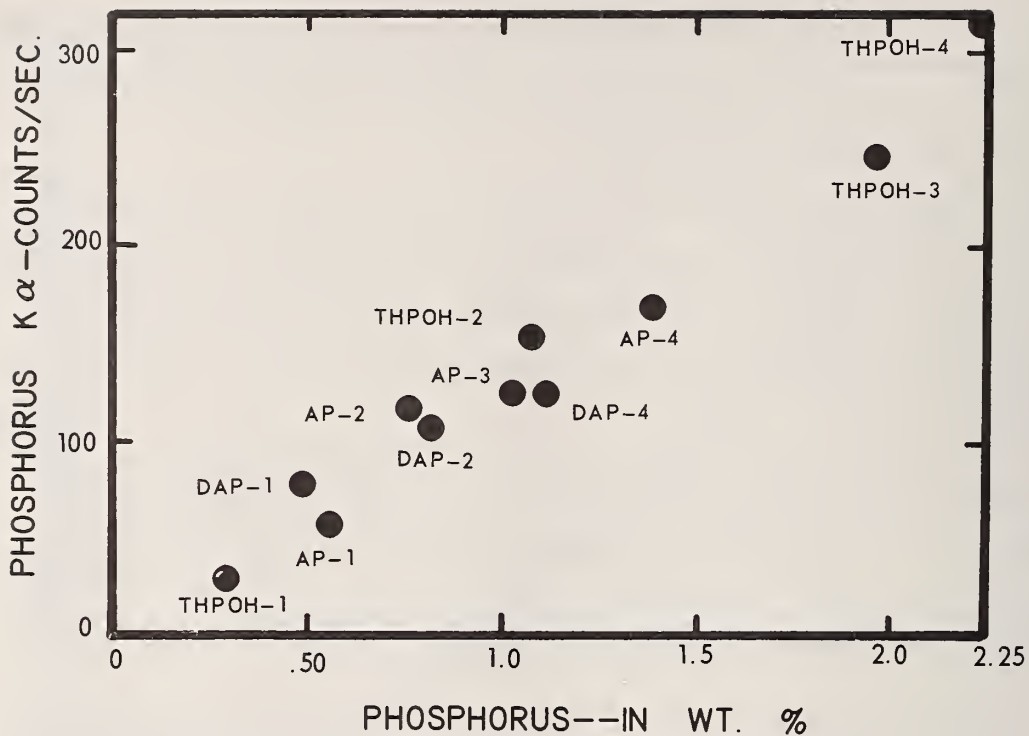


Figure 12. X-ray fluorescence calibration curve for the determination of phosphorus in cloth. The data are for several different treatments and thickness of textile; this may account for part of the scatter observed.

Two other new application areas which we have just begun reviewing are the analysis of air particulate samples and toxic metals in paint films.

F. Other Applications

Fielding Ogburn, Virginia Pennington, and Carole Shriner (from the Metallurgy Division) have continued a project concerning thickness measurements on electroplated metal coatings.

S. D. Rasberry

4. ELECTRON PROBE MICROANALYSIS

A. Instrumental Improvements

1. Scan Driver

A new beam scanning driver has been constructed which takes advantage of the highly stable operational amplifiers and electronics now available. The device incorporates a number of useful control functions which are performed by the operational amplifiers. Easy access is provided to all pertinent summing points. This access will permit inclusion of functions that may be needed in the future. Such needs are expected to arise when the Division computer is interfaced to the microprobe.

The functions included in the present design are as follows:

- a. Translation and rotation of an entire scanning area. See Figures 13 and 14.

- b. Continuous control of magnification (zoom control).

- c. A mirror image - normal image switch to permit inverting the X-sweep direction in the electron probe with respect to the oscilloscope. See Figure 15.

- d. A dash generator to mark the locus used in line scanning. See Figure 16.

- e. A switch for selection of sweep speeds. The available positions are: fixed slow - fixed fast - variable sweep speed.

- f. A vertical-sweep counter control which permits, for purpose of photography, a predetermined number of sweeps, after which the display scope is blanked and an indicator is activated. The range extends from 2 to 99 sweeps.

- g. Provisions for Y-axis-modulation and oblique oscilloscope display (See Figure 17). We have incorporated

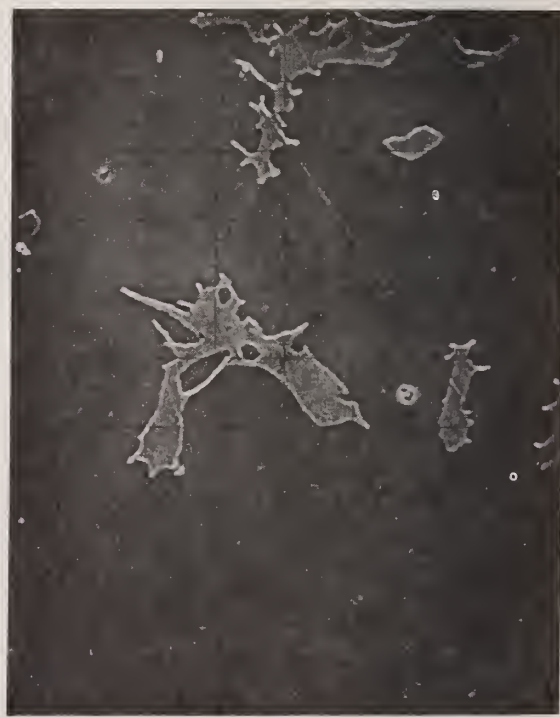
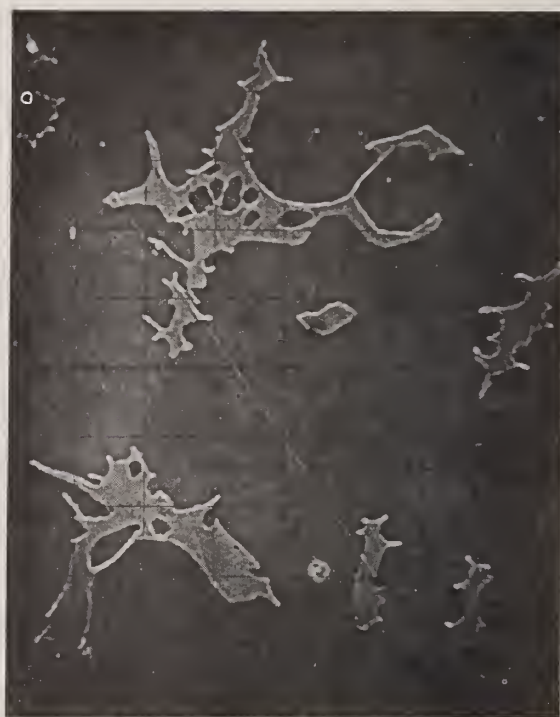


Figure 13. Electromagnetic translation of the field of view. Target current images of a two-phase nickel-aluminum alloy. One large division equal to 66 μm (150 X).

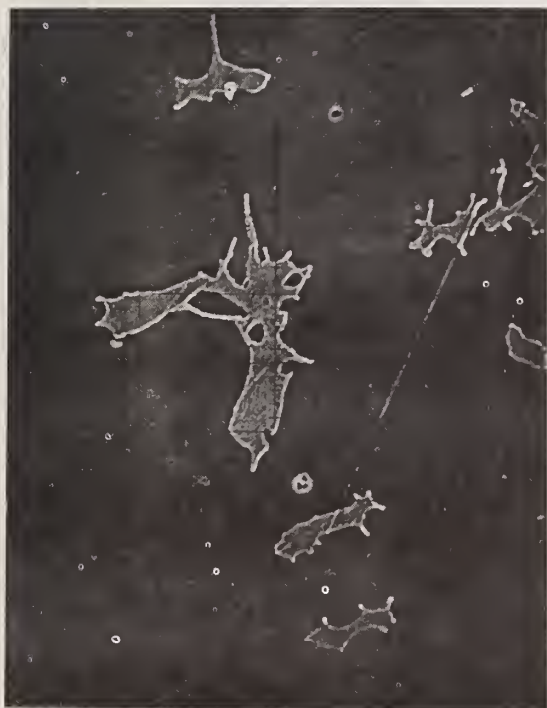
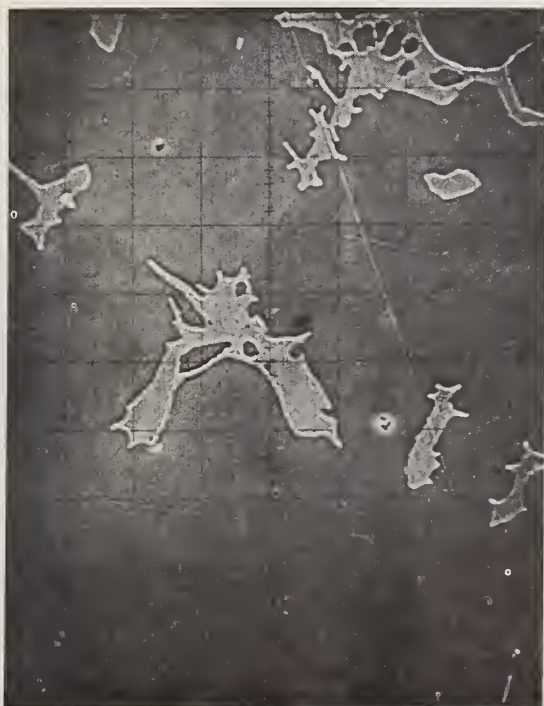


Figure 14. Rotation sequence through steps of 180° (two-step variation between images), same specimen and magnification as Fig. 13.

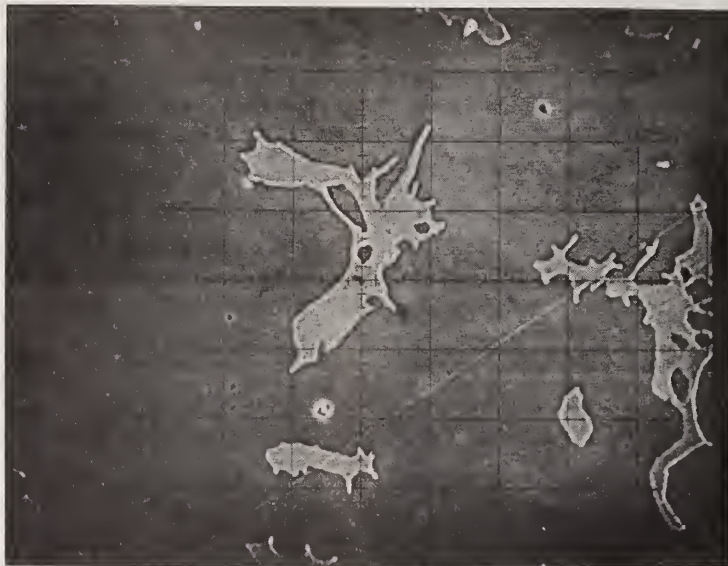
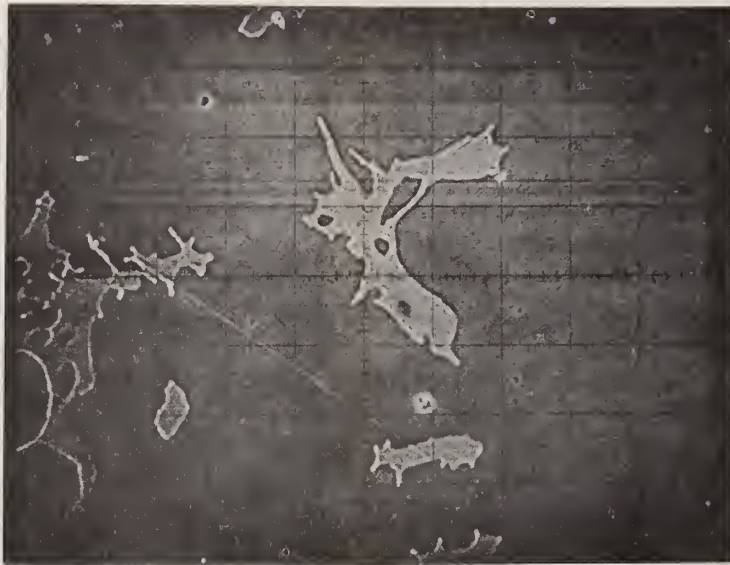


Figure 15. Normal image and mirror image of same view field. Same specimen and magnification as Fig. 13.

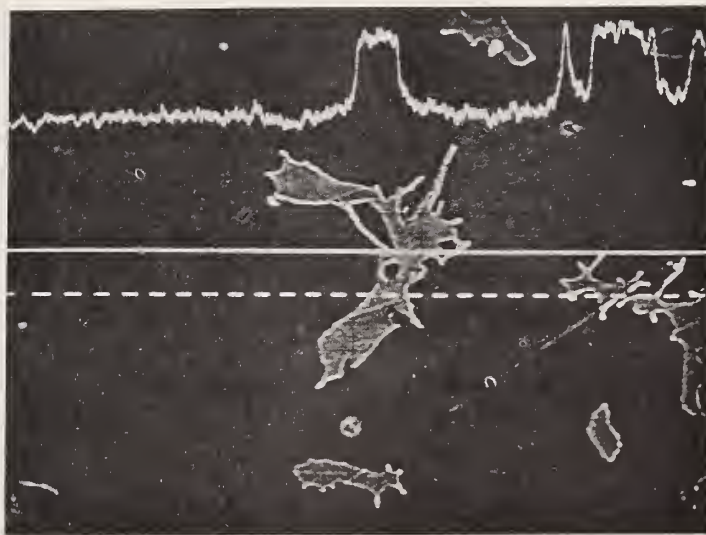


Figure 16. Electronic line scan on the same specimen as Fig. 13, superposed on target current area scan. Full lines show Al $K\alpha$ signal and background; broken line shows location of line scan on the specimen, with respect to the area scan. One large division equal to 66 μm (150 X).

this feature for special cases, although usually a derivative signal brightness modulation and rectangular format are preferred when secondary electron or target current signals are used [15]. X-ray signals from a ratemeter can also be employed to modulate the Y-axis.

The following is a more detailed description of several of the functions.

a. Translation and rotation of an entire area

Electronic translation of the field of scanning, especially at high magnification, simplifies positioning the area selected to be analyzed. It removes the need for mechanical manipulations, which can be cumbersome at high magnification. Rotation is most useful when a line scan is performed. It permits adjusting the angular position of the line scan on the specimen without mechanical manipulation. Rotation is always about the center of the field of view, and independent of translation. Electronic translation and rotation are as easy for the operator at high magnification as the mechanical equivalents are at lower magnification.



Figure 17. Y-axis modulation of target current signal with oblique view-field presentation. Same specimen and area as Fig. 13.

b. Zoom control

The zoom magnification capability, which was available in the original equipment, has been retained in our design. Besides the obvious advantage of continuous control of magnification, at any kilovoltage, the following mode of operation is useful. Since one can increase magnification until no beam deflection occurs in the electron probe, (infinite magnification), one can go from a scanning mode to a static (point-analysis) mode in a continuous fashion. This obviates the need for a separate static-beam control. The advantage of going to a static beam in the above manner lies in the security that one gains by watching the beam scan collapse into the spot selected for analysis.

c. Fast Scanning

There are several advantages in examining a specimen, particularly a large one, by scanning techniques, rather than using the optical microscope of the electron probe. In the first place, the magnification of scanning can be adjusted continuously and quickly over a very wide range. The depth of focus of the scanning image is far larger than that of the optical image, and the quality of electronic image is generally better than that of the optical image, particularly on non-metallic specimens. Furthermore, the oscilloscope scanning image can be observed simultaneously by several persons. However, at slow scanning speeds, the completion of a scanning frame must be obtained every time the position of the area scan on the specimen is changed. Therefore, on the new scanner, we have provided speeds which produce a continuous, coherent picture so that mechanical translation of the specimen is followed instantaneously by the corresponding change of image on the oscilloscope.

The new beam scanner is a self-contained, versatile device of excellent long term stability. It may be used with any X-Y display oscilloscope accepting 10-volt level signals for X-, Y- and Z-axes. It contains most of the imaging and

x-ray selection functions of the microprobe under the control of one rotary switch.

A diagram of the scan driver is located at the end of this publication as Appendix II.

2. Electron Lens and Power Supplies for Higher Beam Resolution

In order to reduce the diameter of the electron beam, we have acquired and installed a new condenser lens of shorter focal length and a new Wehnelt cylinder (grid cap). With these modifications, it is now possible to realize, routinely, probe diameters of $1/4 \mu\text{m}$ at a current of $2 \times 10^{-8} \text{A}$. Previously, our probe diameter, at this current, was $1/2 \mu\text{m}$. At a beam current of 10^{-10}A , these improvements should reduce the beam diameter to 500\AA . However, using this beam intensity for scanning images would require the installation of a secondary electron detector. Such an installation would be impossible without fairly extensive redesigning of the instrument.

We have also constructed new power supplies for both objective and condenser lenses. These supplies are interchangeable and are far more stable than the previous units. Present long-term stability is $\pm 5 \mu\text{A}$ in $.1 \text{ A}$ (50 ppm) after one hour warm-up. This eliminates any perceptible drift in the field strength of the lenses.

3. Residual Gas Analyzer (RGA)

This device (Figure 18), installed on the top of the electron probe tank, permits us to characterize residual gas composition in the electron probe after pump-down. The RGA is a small mass spectrometer that ionizes residual gases by means of a heated filament. The range extends from mass to charge ratios of 2 to 100.

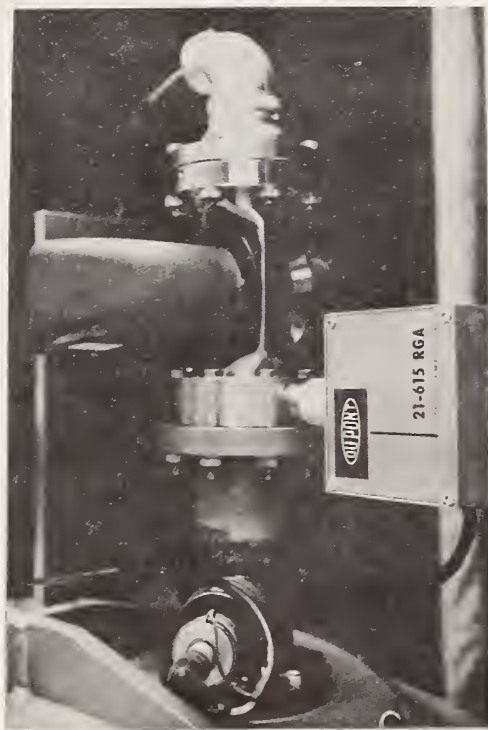


Figure 18. Residual gas analyzer mounted on top of the tank of the electron probe microanalyzer.

A useful observation made with this device concerns the pump-down cycle of the microprobe. Bleeding atmospheric air into the sample chamber, and especially the main tank, leaves a considerable amount of water in the system. This water adheres tenaciously to the walls, requiring up to 24 hours to pump out. Water is known to be a significant cause of corrosion of the filament. Hence, we now eliminate the water contamination by venting dry nitrogen into the sample chamber, rather than air. Figure 19a shows the magnitude of the water signal immediately after pumping down the sample chamber (which had been vented with air). This signal exceeds those of all other constituents. After 24 hours of pumping, the water signal is still fairly large (Figure 19b). The argon shown in the spectra is due to leaking of the filling (Ar, 10% CH₄) of the thin-window x-ray detectors.

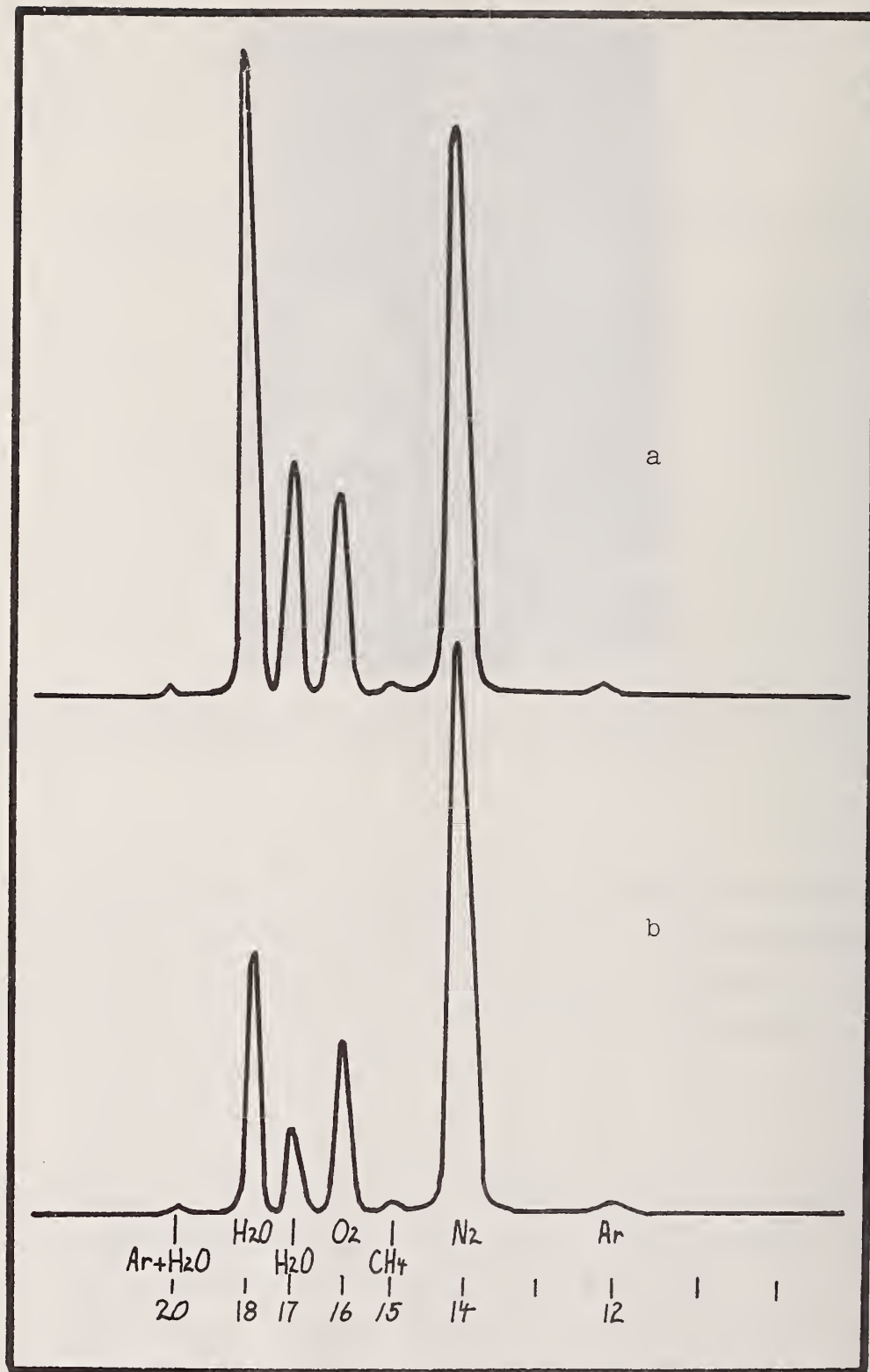


Figure 19. Residual gas spectra of the atmosphere within the tank; immediately after venting the sample chamber with air (a), and after 24 hours of continuous pumping (b).

An initial attempt at observing, with the RGA, ions freed from the sample surface due to impact of the electron beam met with no success. The samples used were organics and salts. Other investigators successfully applied this technique in rare gas determinations in stoney meteorites [16], and lunar material [17].

B. Scanning Techniques and Sample Preparation for Small Particles and Biological Thin Cuts

In the past, most of our research has been focused on large, flat specimens of thickness exceeding the depth of electron penetration. This is the form of specimen in which most of the metallurgical and mineral materials are presented to the electron probe; quantitative techniques are usually based on the assumption that the specimen is flat and of "infinite" depth and width.

There are, however, areas of application in which such a specimen configuration is impossible. The analysis of small particles (in this context, of diameter below 10 μm) is of great significance, for instance, in studies of air pollution. The importance of the analysis of thin films (thickness less than 1 μm) in many technological devices is well recognized. An especially difficult case is presented by biological materials. The low density of soft tissue renders the paths of penetration of the electron undesirably large at the usual acceleration potentials. One can increase resolution in spatial dimensions by analyzing thin sections; such sections are also required in the customary microscopic techniques (light microscopy of stained sections and transmission electron microscopy). But such thin sections, particularly if not stained with heavy elements, show poor contrast in the usual target-current or secondary-electron imaging procedures in the electron probe. It is for this

reason that costly transmission electron microscopy attachments [18-20] are frequently used for biological specimens.

The analysis of biological materials is beset by two further difficulties: biological tissues are easily damaged by the heat which is produced by the impinging electron beam; and the x-ray signals one obtains are generally weak, since elements other than carbon, hydrogen, oxygen, and nitrogen are present at low concentrations.

We have started a research program to explore the conditions of analysis of small particles and thin films. The ultimate goal of such a program ought to be the development of quantitative methods of analysis. However, a particle or a detail of a histological specimen cannot be analyzed unless they can be found in the electron probe; after locating the feature, we still need conditions of specimen preparation and mounting, and of excitation and x-ray detection, which permit the reception of signals of sufficient intensity without destruction of the specimen. We must therefore begin by examining techniques of imaging and contrast production, and then pay attention to the attainable x-ray intensities, before considering the more complex problems of quantitation. In this preliminary phase, we must reexamine matters already covered by other investigators; therefore, we do not claim, at this stage, priority or originality.

1. Handling of Particles

Quantitative analysis of dust particles is complicated by their unknown geometry, since the smaller particles do not stop all electrons penetrating them. Besides backscatter, we have thus to consider the transmission of electrons.

Another practical problem arises from the electrostatic charging of nonconductive particles. The charges may create forces which not only may deviate or repel the electron beam, but also may dislodge the particle if it is not firmly

mounted. Furthermore, a particle may suffer a large rise in temperature if it or its surroundings have low thermal conductivity and specific heat. These problems place stringent requirements on the techniques for mounting particles, since these must be firmly held and have good thermal contact with the mounting medium. Yet, the medium must not be too heavy so as to significantly absorb the impinging electrons or the x-rays emitted from the particle, or to emit continuous or characteristic x-rays at a level which would obscure the weak signals from the particle. Further, the electrical resistance from the particle to ground should not exceed the order of $10^9 \Omega$.

A technique in which particles are mounted in very thin films of formvar or collodion is presently under development. The particles are entirely enclosed in a thin film as shown in Figure 20. This creates good thermal and electrical contact, while it does not impair electron or x-ray transmission. This film is mounted in such a manner that the electrons traversing it travel more than 20 mm before impinging upon an absorber of low atomic number. This arrangement practically eliminates the detection of background radiation other than the continuum generated in the particle itself.



Figure 20. Diagram of particle mounted within thin organic film.

Separate paths into the imaging electronics are provided for the electrons absorbed within the specimen and for those transmitted through the specimen and collected by the absorber. This permits imaging configurations of high contrast. The parameters regulating the intensity of x-ray emission will be studied in more detail at a later date.

The film is highly transparent to light, and the specimens can be examined with a standard microscope and then transferred to the electron probe without changing the mounting.

The preparation, as developed to date, is as follows. A 10% formvar (powder) - 90% ethylene dichloride (by weight) solution is prepared and the particles are suspended in this slightly viscous liquid. One drop of the solution is now placed onto a pure water surface and a very thin formvar film forms instantly, extending over several square centimeters of the water surface. The particulates are entrapped in the film.

A common fiber washer, with an inside diameter of 1/4 inch, is placed on the film. By delicately pressing the washer into the film, a bond is made. After trimming off the film outside the washer, it may be lifted from the surface of the water.

Electrical conductivity is provided by evaporating carbon onto both sides of the film, with the bottom side receiving a somewhat heavier coat than the top. The carbon film also improves the thermal and mechanical properties of the formvar film.

An analogous procedure is followed if collodion rather than formvar is used. A 50% ethyl alcohol - 50% Flexible Collodion U.S.P. solution seems to be adequate in this case. The chief difference between the two materials is that formvar films are more uniform in thickness while collodion tends to develop a fibrous structure. A scanning electron micrograph of a collodion film is shown in Figure 21.



Figure 21. Absorbed electron scanning image of fly ash particles mounted in collodion. Magnification: 25 $\mu\text{m}/\text{cm}$.

The x-ray signals from four randomly chosen particles in the area of Figure 22 (small fly ash in collodion) are shown in the accompanying graph. The elements present are labeled on the abscissa. The ordinate is in arbitrary intensity units.

2. Analysis of Biological Specimens

In the study of biological specimens, the observer must distinguish and recognize microscopical features of interest before attempting to analyze them. The ease of observation and orientation frequently determines success or failure of biological microanalysis. Typically, the biologist has observed a thin tissue section with either the help of optical microscopy or of transmission electron microscopy. The first task in electron probe microanalysis is to identify locations and features first observed with the above mentioned tools.

While optical microscopes are incorporated in the electron probe, their quality is usually unsatisfactory for histological observation, owing to spacial limitations. Besides, the investigation of the distribution of elements in water-soluble form precludes the use of staining procedures. The same objection must frequently be raised to the use of staining with heavy elements as sometimes employed in transmission electron microscopy. There is undoubtedly a demand for a scanning procedure which provides a sub-micron resolution and sufficient contrast to be used with unstained preparations of thickness below one micron.

Special electron probe instruments containing optical microscopes of high resolution [21] or provisions for transmission electron microscopy [18-20] are now available. Still, in view of the wide diffusion of standard electron probes, it is worthwhile to experiment with alternative solutions which are available with the standard instrument. The extensive use of scanning electron microscopy in electron probe microanalysis suggests that such techniques be investigated. However, as stated before, in order to achieve the desirable spatial resolution, we are frequently forced to use thin sections; the contrast obtainable from such specimens, particularly if unstained, is insufficient if either target current or secondary electron signals are employed.

We are presently experimenting with scanning electron microscopy using transmitted current as a signal. The specimen is mounted on a thin film, as advocated by Hall [22]; this is a prerequisite for the observation of low concentrations which require maintaining a low x-ray background. The contrast in the observation of such thin specimens by transmission electron microscopy is created, not by absorption, but by scattering of electrons [23]. The same principle can be applied to the observation of specimens which are scanned with an electron beam. In this case, the undeflected beam is

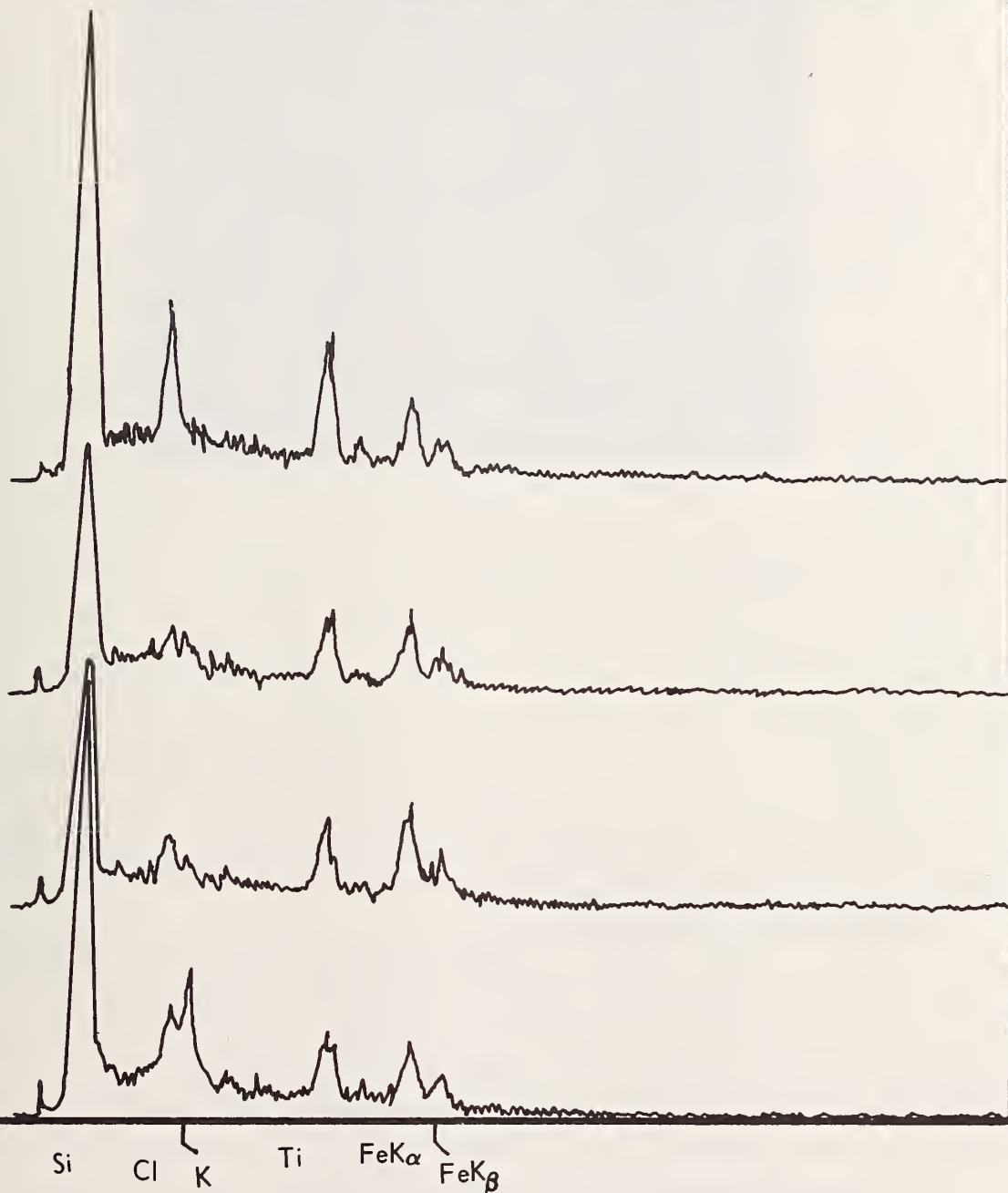


Figure 22. Pulse-height spectra of four fly ash particles mounted on collodion film, obtained with lithium-drifted silicon detector. Abscissa represents photon energy, ordinate represents x-ray intensity on an arbitrary scale.

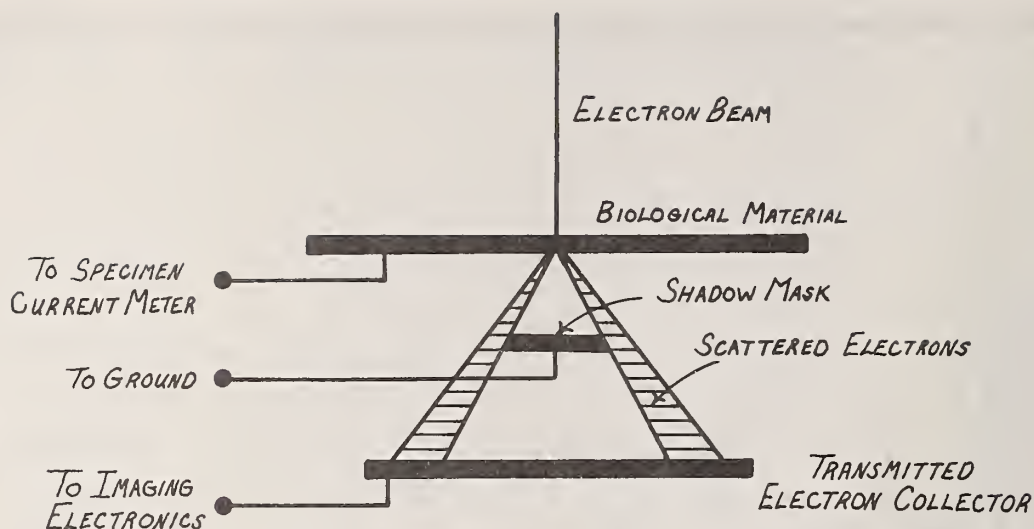


Figure 23. Schematics of specimen holder for the detection of scattered (transmitted) electrons.

intercepted and led to ground; the electrons which were scattered out of their original direction are collected in a ring-shaped collector, and used to form the signal. Figure 23 schematically shows a specimen holder we have developed for this purpose. An electron micrograph prepared with this technique is shown in Figure 24.

We mount the biological tissue sections on thin organic films, such as collodion, formvar, or stretched polypropylene. The microtome cuts can be floated on water and picked up with such a film, stretched over a small fiber washer. After the assembly has dried, both sides of the film are coated with carbon.

Satisfactory contrast can be obtained by this method from unstained tissue sections of thickness below 1 μm . Since supporting grids are avoided, and since the supporting film is very thin, the x-ray background is also very low, and there are no characteristic lines present which are not generated within the specimen.

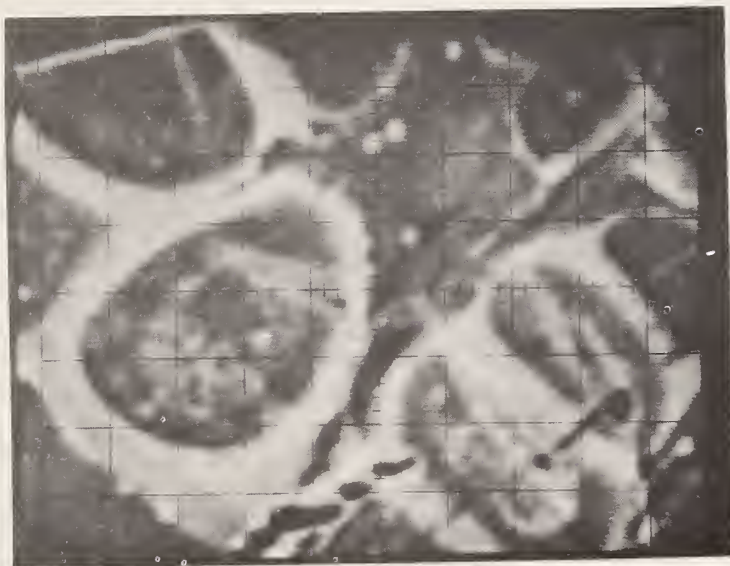


Figure 24. Scanning transmission electron micrograph of unstained cartilage tissue obtained with the device shown in Fig. 23. Operating voltage: 20 keV. Magnification: 6.6 $\mu\text{m}/\text{cm}$ (1500 X).

C. Quantitative Analysis

Research in quantitative electron probe analysis this fiscal year was a continuation of the investigations initiated last year [6]. 1. The study of the background corrections was expanded to include measurements of the limit of detection. 2. The theoretical study of the corrections for fluorescence due to both characteristic lines and continuous radiation has been complemented by the measurements of the Standard Reference Materials (SRM's 481 and 482) of Au-Ag and Au-Cu alloys [8]. 3. The documentation of the computer program, COR, extensively described in our last report [6], has been completed and the program MULTI 8 has been rewritten in Fortran IV. 4. The practical aspects of determining the compositions of phases in binary alloys have been examined.

We will now comment, in more detail, on some aspects of the research outlined above.

1. Limit of Detection

Electron probe microanalysis is typically a micro-analytical but not a trace analytical technique. Most proposed limits of detection are based on the assumption that no errors other than those inherent in the Poissonian counting statistics are present. However, as an investigator increases his efforts to lower the limit of detection, non-Poissonian errors become more prevalent, and he is left with an optimistic estimate rather than a true measure of detection limits. Thus, an estimate of the experimental standard deviation of the background is a more appropriate expression of statistical precision at the trace level than the Poissonian estimate of standard deviation.

In an effort to determine the experimental standard deviation of the background on realistic specimens, we have measured the intensity of the $\text{CrK}\alpha$ x-ray line in a series of low alloy steels. The Standard Reference Materials 461 through 468 were chosen for this purpose for two reasons. First, these steels have been well analyzed and range in composition from 0.004 weight percent chromium to 0.74 weight percent chromium. There are many other elements present in these steels; however, all of them are low in concentration and were not considered in our measurements. Second, and of equal importance for microanalysis, these materials appear to be homogeneous on a micron level. Standard Reference Materials 461 and 463 had been previously investigated by electron probe microanalysis and by quantitative metallographic techniques [24-25]. It was then concluded that they are sufficiently homogeneous so that any presently available microanalytical technique can be carried out with little change of inaccuracy due to inhomogeneity. Multiple measurements on the other Standard Reference Materials in this

series indicate that they are equally homogeneous; however, studies should be performed on these alloys to determine the homogeneity of each Standard Reference Material.

The experimental conditions were chosen to match those used typically on the electron probe. The target current was 2×10^{-8} amps at 20 keV and the counting time was 20 sec for each data point. Some of the data obtained are plotted in Figure 25. The results were fit to the line

$$k = mC + b \quad (1)$$

by the method of least squares [26], where:

k = CrK α intensity (total counts)

m = slope

C = mass fraction (concentration) of chromium in specimen and

b = background (k -intercept at $C=0$).

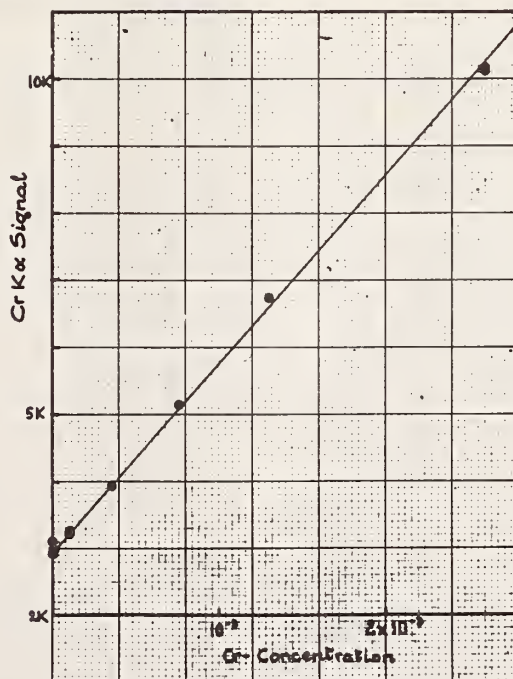


Figure 25. Cr K α signal from low-alloy steels. Vertical signal shows number of counts obtained in 20 sec.

The estimate of the standard deviation of the background (s_b) could then be calculated with the following equation [26]:

$$s_b = s_k \sqrt{\frac{1}{n} + \frac{\left(\frac{\sum C_i}{n}\right)^2}{\sum C_i^2 - \frac{(\sum C_i)^2}{n}}} \quad (2)$$

where s_k = estimate of the standard deviation of k

n = number of data points

and C_i = concentration at point i .

The summations in equation 2 are for values of i from 1 to n . The result is an estimate of the standard deviation of the x-ray signal intensity obtained when the element is absent ($C=0$, $k=b$). In order to determine the estimate of the standard deviation of the concentration, it is necessary to divide s_b by the slope of the line (m):

$$s_c = \frac{s_b}{m} \quad , \quad (3)$$

where s_c is an estimate of the standard deviation of a single measurement of the concentration at the background. Different authors have defined the limit of detection in a variety of ways; however, most definitions can easily be related to the estimate of the standard deviation (s_c) defined above. For one case of 20 data points, the limit of detection (s_c) for chromium in iron was calculated to be 0.008 weight percent.

2. Further Measurements on Standard Reference Materials

Our efforts to improve the accuracy of quantitative electron probe microanalysis have been in two directions. The first involves careful measurements on well characterized materials, as described in this Section, and the second is

concerned with developing the best possible computer program for calculating the correction procedures, as described in the following Section.

Intensity ratios were measured for $\text{CuK}\alpha$, $\text{CuL}\alpha$, $\text{AuM}\alpha$, $\text{AuL}\alpha$ and $\text{AuL}\beta$ in the Cu-Au system Standard Reference Materials, and for $\text{AgL}\alpha$, $\text{AgL}\beta$, $\text{AuM}\alpha$ and $\text{AuL}\alpha$ in the Ag-Au system Standard Reference Materials at 5, 10, 15, 20, 30, 40, and 48.5 keV. An example of the results is shown in Figure 26 where the ratios of the relative intensities to the concentrations are plotted versus the relative intensities for $\text{CuK}\alpha$.

Comparisons of theoretically calculated intensity ratios with the experimentally measured ratios are being made in hopes of improving the calculations. Data on $\text{CuK}\alpha$ obtained from the 40Cu-60Au alloy are shown in Figure 27. The complete results of these measurements are in the process of being published as an NBS Special Publication [9].

3. Computer Programs

The above mentioned computer programs, COR and MULTI 8 have been used for the calculations mentioned in Section 2. Both of these programs are to appear shortly in a publication describing the calculation procedures used and explaining how to use the programs. The program, COR, has been extensively tested, documented, and flow-sheets have been drawn.

MULTI 8 is a comparatively short computer program written in the BASIC language for the correction of electron probe microanalyzer x-ray data on a time-shared computer. The following comments briefly outline the calculations performed by the program. The generation equation (atomic number correction) follows a modified procedure of Poole and Thomas [27]. The stopping power is calculated from the Bethe equation [28], employing the mean ionization potentials proposed by Berger and Seltzer [29]. The backscatter losses are

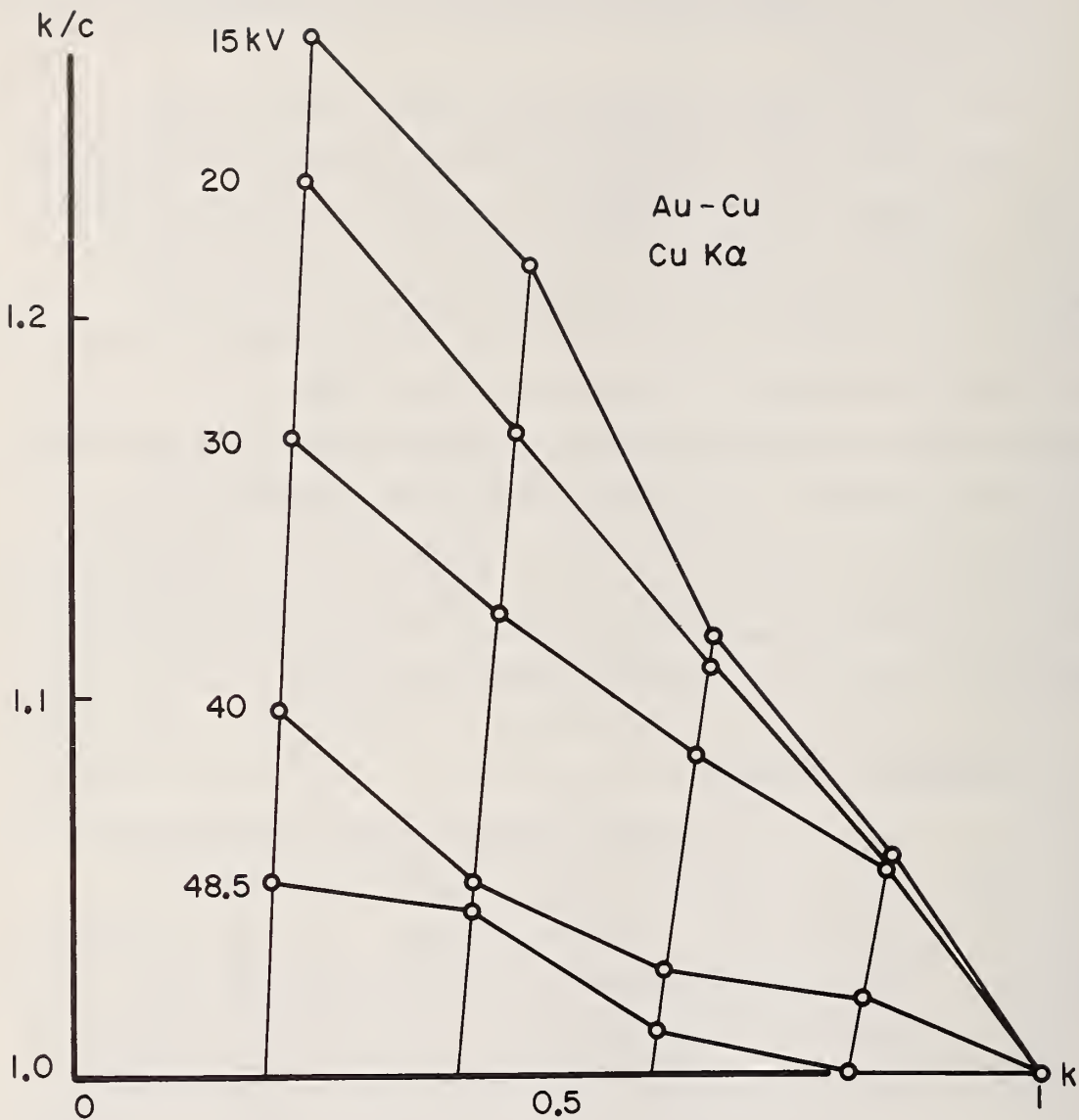


Figure 26. The copper $K\alpha$ measurements in gold-copper binaries are represented by plotting the ratio k/C on the ordinate, and k on the abscissa. The thin, almost vertical lines connect points corresponding to the same composition, which can be read on the horizontal scale, where $k=C$.

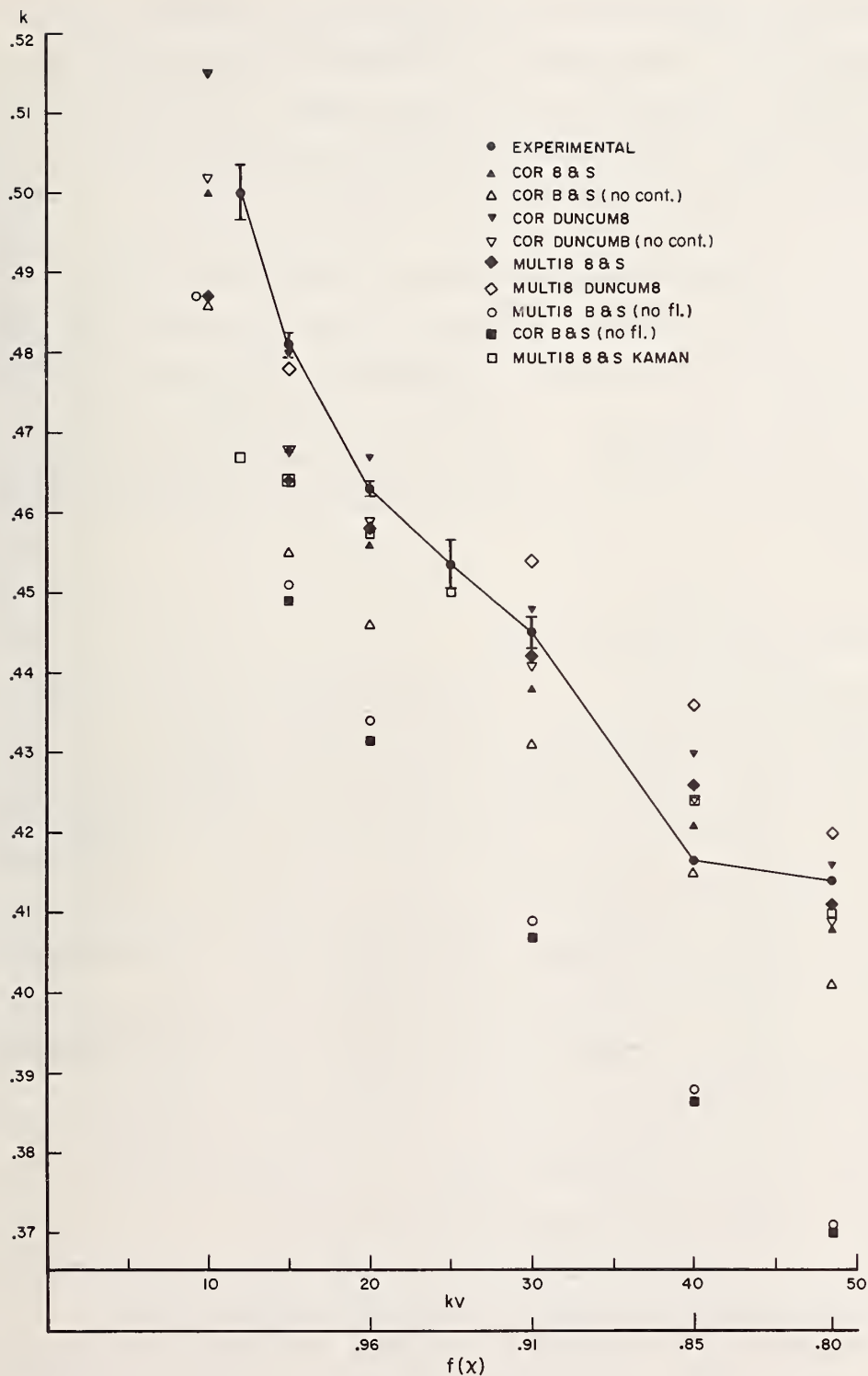


Figure 27. Experimental and theoretical intensity ratios of Cu $K\alpha$ for a nominally Au₆₀-Cu₄₀ alloy. Note the spread of theoretical predictions depending on the choice of theory and parameters. (For a detailed discussion on this subject see [9]).

calculated by a procedure advocated by Duncumb and Reed [30]. The calculation of the absorption of primary x-rays uses the modification by Heinrich [31] of the procedure of Philibert [32] and Duncumb [33]. The fluorescence by characteristic lines is calculated by the method of Reed [34]. There is no provision for correcting the effects of fluorescence produced by continuous radiation. The iteration procedure is a modification [31] of that proposed by Criss and Birks [35]. Since we use this program extensively for calculating the electron probe results, we rewrote it in Fortran IV for the Division's new EMR 6135 computer. The rewriting of this program also allowed us to gain some experience in programming the new computer.

4. Studies on Binary Alloys

In cooperation with Mr. R. M. Waterstrat, of the Dental Research Group, we have compiled the following list of advantages of the use of an electron probe microanalyzer for determining the compositions of phase boundaries in binary alloys, with suggestions concerning this technique. These boundaries have usually been determined by either optical methods [36] or by x-ray diffraction methods [37]. The major difficulty with both of these techniques is the large number of specimens required to determine a particular phase boundary. Our observations are based on extensive microprobe analyses of the binary alloys chromium-platinum, chromium-iridium, chromium-rhodium and vanadium-platinum. The results of this work may be found in an NBS report [38].

Two types of specimens may be examined with the electron probe to directly yield the phase boundary compositions. In the past, solid state diffusion couples have been studied with the electron probe microanalyzer; in many instances, with reasonable success [39]. This method is attractive, since it requires only one specimen for an entire phase

diagram. However, sometimes the phase regions are too narrow to obtain good quantitative results, and some phases may be missing entirely from the diffusion couple. The other type of specimen, discussed below, is annealed and quenched from within a two phase region in the same manner as for the optical method mentioned above.

All the specimens we studied were formed by arc-melting the two pure components together into a button of the particular composition required. These buttons are then annealed at various controlled temperatures at which information is required, and they are quenched. The resulting button is cross-sectioned, mounted in bakelite and metallographically polished. The electron probe microanalyzer may then be used to examine the phases present. This technique has the following advantages over the older methods mentioned above:

- a. Analyses may be easily performed on material located near the center of a button. Material near the outer edge of a button could have changed composition due to preferential vaporization of one component during arc-melting or annealing.

- b. Small oxide inclusions which may form during melting can be avoided during analysis.

- c. Specimens which may have become contaminated can easily be tested for the impurities.

- d. The compositions of the phase boundaries on either side of a particular specimen can be determined by analyzing both phases in that specimen. As a result, fewer specimens are required than are necessary when either optical metallography or x-ray diffraction is used.

- e. Broken areas of brittle specimens and holes in porous specimens can easily be avoided. This could possibly save an otherwise unusable specimen.

In order to obtain the best results from an electron probe microanalysis, the following suggestions are offered.

a. A good optical examination should be made prior to electron probe microanalysis. One must beware of decompositions into fine-structured material such as an eutectoid. Very fine precipitates may be missed either optically or with the microprobe.

b. Specimens near a eutectic composition should not be used. Eutectics are usually too fine-grained to yield good quantitative analyses. Near a phase boundary, the minor phase forms larger grains and is more easily analyzed.

c. For dependable results, the phases should be evenly distributed throughout the specimen and all grains of the same phase should have the same composition.

D. Service Analyses

We have performed a large number of service analyses on a wide variety of materials, including the following.

1. Variations in concentration of several silicate minerals were investigated in thin sections of lunar materials from Apollo 11, 12 and 14 in a cooperative program with NASA Goddard.

2. Analysis on various materials affected by corrosion or other failure processes. These include:

- a. Cracks in a helicopter part
- b. A section removed from a part of a ruptured tank car
- c. A scab on an aluminum alloy section from a ruptured liquid-oxygen cargo tank
- d. Corrosion of an aluminum aircraft propeller
- e. Oxidic surface on test specimens of TD-nickel heat shields for a simulated atmospheric reentry vehicle

3. Binary two-phase alloys: Very accurate measurements were performed on the systems chromium-iridium and chromium-rhodium as part of a program to investigate the respective equilibrium phase diagrams [38]. The compositions and homogeneity of tungsten-rhenium lamp wires were also measured.

4. A variety of single crystals were analyzed for composition and for variations in composition. These include:

- a. Lead-tin-tellurium crystals
- b. TlTe and TlBiTe₂ crystals
- c. A β -Ca₃(PO₄)₂ micro-sphere crystal

5. Extensive analyses were performed to determine the compositions and distributions of inclusions in the steels, SRM 661-5. This was done in order to ascertain their suitability as microanalytical standards. At the present time, the certificates on the Standard Reference Materials are being prepared.

6. Qualitative analyses of fine particulates such as fly ash and air pollutants have been performed.

7. Other miscellaneous investigations included the quantitative analyses of evaporated thin films of various alloys, variation in composition around a laser lesion in glass, the homogeneity of an In-Ga alloy, and qualitative analyses of "polywater", solder on a circuit board, crystals on a filter paper, a surface smear on aluminum oxide, ink on counterfeit money, and the calcium distribution in a human bone.

C. E. Fiori, R. L. Myklebust

5. PRECONCENTRATION TECHNIQUES

In previous Annual Reports of this Section's activities [4-6], separation and preconcentration procedures have been reported for determining trace elements in a variety of materials. This year's focus has been placed on developing procedures for analyzing important types of environmental samples and certifying several new Standard Reference Materials. Examples of these applications will be given in some detail to illustrate the utility of the techniques.

A. The Interaction of Nitrilotriacetic Acid (NTA) Solution with River Sediments

The sodium salt of nitrilotriacetic acid (NTA) was one of the materials proposed by detergent manufacturers to replace polyphosphates in detergents. However, because of its chelating properties, dilute solutions of NTA could potentially extract and solubilize metallic elements contained in the suspended matter and sediments of bodies of water. By this process, toxic metals present in a relatively innocuous form could be converted to a bio-assimilable form. Biological retention of these metals in the food chain could result in concentrations occurring in food fish that would be harmful for human consumption.

To investigate these potential ecological faults of NTA, the Federal Water Quality Administration, (now Water Quality Office, Environmental Protection Agency) established a project at NBS. The basic study in this investigation was the interaction of sediments with very dilute NTA solutions under conditions reasonably to be expected in bodies of water. Trace analytical techniques were used to determine the chelating action of NTA.

A number of river and coastal sediments were obtained, from which samples were taken for qualitative optical emission analysis by Mrs. M. Darr. These analyses permitted the selection of sediments having elements of special interest at diverse concentrations, for equilibration studies with water and with 20-ppm NTA solutions. R. A. Paulson, of the Microchemical Analysis Section, performed the equilibrations by using a mechanical shaker to agitate the sediments with water and 20-ppm NTA solutions. Following agitation, the solutions were centrifuged.

An isotope dilution, preconcentration technique, using spark-source mass spectrometry (ID-SSMS), was one of the methods developed to analyze these solutions. Previous applications of this method have been described [40-42]. In the ID-SSMS method, the concentration of an element in a matrix is determined from the change produced in its natural isotopic composition by the addition of a known quantity of the same element, the isotopic composition of which has been artificially altered (spike). Since an isotopic ratio of the final isotopically equilibrated material is measured to obtain the concentration, the results are not invalidated by losses of the trace element analytes. By the use of preconcentration techniques and multiple spikings, a number of trace elements can be determined simultaneously with high sensitivity. The results are calculated using:

$$C = \frac{W K (A_{sp} - B_{sp} R)}{M (BR - A)},$$

where C is the concentration in ppm ($\mu\text{g/g}$), W is the weight of isotopically enriched materials (spike) added in μg , M is the weight of sample in g, A and B are the natural abundances of the analyte isotopes a and b, A_{sp} and B_{sp} are the abundances of isotopes a and b in the spike, R is the measured altered ratio of isotope a to isotope b, and K is the ratio of the natural atomic weight to the atomic weight of the spike.

In the method developed, information was obtained on the concentrations of fourteen elements in the solutions from the equilibrations of the sediments with water and 20 ppm NTA solutions. These elements were: Ag, Ba, Cd, Cr, Cu, Fe, Hg, Mo, Ni, Pb, Sb, Sn, Sr, and Zn. Solutions of the enriched isotope materials were prepared for the elements to be determined. Chemically compatible solutions were combined and volumetric additions of these "multiple-spike" solutions were introduced into volumetric flasks. The flasks were made to volume by adding portions of the water (0 ppm NTA) and 20 ppm NTA solutions that had been equilibrated with the sediments. Aliquots of these spiked samples were pipetted into small quartz flasks and 0.3 ml of a 1:1 nitric-perchloric acid mixture were added to each flask. The acids were of high-purity grade. After evaporating the solutions in a "clean environment chamber" [40], the solutions were heated further to HClO_4 fumes. This step destroyed the NTA and equilibrated the analytes with the enriched isotope spikes. The residue was dissolved in distilled water and the resulting solution was transferred to a Teflon electrolysis cell. The isotopically altered analytes were electrodeposited onto two high-purity gold wire cathodes connected in parallel. Two gold wires served as the anodes. The cathodes were sparked in the spark-source mass spectrograph and the spectra were photographically recorded. For the initial samples, it was found that the solutions had been "over-spiked," that is, the concentrations of the trace elements were appreciably lower than anticipated. Consequently, to obtain suitable isotope ratios for more accurate measurement, aliquots of the spiked samples were diluted with known volumes of the sample solutions and the procedure was repeated. The results, in micrograms per milliliter of solution, were computed from the isotope dilution equations. Method blank determinations were made under the same experimental conditions using the same volumes of acids.

Tables 3 and 4 list the isotope dilution-spark source mass spectrographic determinations of the fourteen trace elements in water (0 ppm NTA) and 20 ppm NTA solutions equilibrated with sediments. The elemental determinations were made simultaneously in each sample. These data, together with those obtained in the Division using several other analytical techniques, formed the basis for the conclusions presented in a formal report to the Environmental Protection Agency.

Table 3. Concentrations in micrograms of element per milliliter of solution which had been interacted with river bottom sediment (Pb, Hg, Sn, Cd, Zn, Cu and Fe)

<u>Sample Designation</u>	<u>ppm NTA</u>	<u>Pb</u>	<u>Hg</u>	<u>Sn</u>	<u>Cd</u>	<u>Zn</u>	<u>Cu</u>	<u>Fe</u>
#14	0	0.06	<.01	0.002	<.001	0.03	0.02	0.3
pH 9	20	.04	<.01	.002	<.001	.02	.02	.6
#15	0	.03	0.1	<.01	0.002	.02	.04	.5
pH 7	20	.08	.1	<.01	.007	.1	.02	.5
#16	0	.09	.03	.02	.001	.05	.04	4
pH 8.2	20	.06	.01	.003	.001	.07	.02	2
#22	0	.03	.2	<.004	<.001	.03	.03	1
pH 7	20	.02	.2	<.004	<.005	.04	.03	1
#34	0	.11	.01	.002	.001	.06	.020	1
pH 9	20	.12	.01	.001	.002	.07	.02 ₆	1
#34	0	.2	.2	<.002	<.005	.08	.02	1.4
pH 7	20	.1	.2	--	--	.05	.02	1.5
#35	0	.1	.01	<.001	.002	.08	.02	2
pH 7.7	20	.2	<.01	<.001	.002	.5	.03	1

Table 4. Concentrations in micrograms of element per milliliter of solution which had been interacted with river bottom sediment (Ba, Sb, Mo, Sr, Cr, Ni and Ag)

<u>Sample Designation</u>	<u>ppm NTA</u>	<u>Ba</u>	<u>Sb</u>	<u>Mo</u>	<u>Sr</u>	<u>Cr</u>	<u>Ni</u>	<u>Ag</u>
#14	0	0.06	0.02	0.2	1.1	--	0.03	<.001
pH 9	20	.06	.02	.1	1.2	0.2	.04	<.001
#15	0	.07	--	--	.3	.04	.01	<.002
pH 7	20	.1	--	--	.4	.05	.2	<.001
#16	0	--	.004	.05	--	.1	.06	0.006
pH 8.2	20	--	.004	.03	--	.1	.1 ₅	.001
#22	<0	<.1	--	.03	.02	.03	.01	<.001
pH 7	20	<.1	--	--	.09	.3	.06	<.001
#34	0	--	.001	<.003	.3	--	--	<.001
pH 9	20	.04	.001	.006	.3	--	--	<.001
#34	0	<.03	--	--	.2	.02	.01	<.001
pH 7	20	<.03	--	<.004	.2	.006	.08	--
#35	0	.2	.001	.003	--	.1	.04	<.001
pH 7.7	20	--	.001	.002	--	.1	.1 ₅	<.001

B. Orchard Leaves, Standard Reference Material 1571

1. Determination of Fe, Pb, Zn, Cu, Ni, and Se

The concentrations of certain elements in leaf samples from fruit trees are important in diagnosing nutrient disorders and suggesting cultural treatment [43]. Other elements are also of interest. For these analyses, rapid instrumental

methods are generally used. Synthesized standards are often used to calibrate the instrumental response. However, more reliable results can be obtained when a botanical matrix with reliable concentration values is used for the calibration; and, such a Standard Reference Material can be used to check for bias in the analytical procedure. In making inter-laboratory comparisons of the results obtained on the analysis of kale powder, Bowen [44] listed a number of elements for which the results from different laboratories were in disagreement. "Gross discrepancies" were reported for nickel and mercury.

We have developed a preconcentration ID-SSMS method for simultaneously determining Ni, Fe, Pb, Zn, Cu, and Se in a ground orchard-leaf material subsequently issued as Standard Reference Material 1571. Because of its volatility, mercury was determined separately by a special ID-SSMS procedure. In one of the procedures, enriched-isotope spikes of Fe, Pb, Zn, Cu, Ni, and Se were added to samples which were oxidized with nitric and perchloric acids. The solutions were then evaporated to dryness to remove the acids. After adding a small amount of water, the equilibrated trace elements from an aliquot of the solution were electrodeposited on high-purity gold wire electrodes. The wires were sparked in the mass spectrograph and the spectra were photographically recorded. Results were computed from the measured isotopic ratios using the general isotope dilution equation. These results are shown in Table 5. As part of the method, the concentrations of the spike solutions were verified and system blanks were determined.

During the course of the analysis, a white residue was observed after destruction of the organic matter. This residue was approximately 0.4% by weight. A qualitative optical-emission analysis by Mrs. V. C. Stewart indicated that it contained mainly aluminum and silicon. Iron and

Table 5. Average concentrations in the solution obtained from wet-ashing one-gram samples of Orchard Leaves SRM 1571 - determined by isotope dilution spark-source mass spectrometry

<u>Element</u>	<u>Average Conc.^a, ppm by wt.</u>
Iron	278 \pm 43
Lead	43 \pm 4
Zinc	28 \pm 3
Copper	12 \pm 2
Nickel	1.2 \pm 0.2
Selenium	0.08 \pm 0.02

^aUncertainty is expressed as the 95% confidence limits of a single determination.

copper were estimated to be 0.1 to 1%, and 0.001 to 0.01% respectively of the residue. The most sensitive spectral lines were not detected for the other elements being determined by ID-SSMS. Selenium is not evaluated in the optical emission procedure used.

2. Determination of Mercury

A preconcentration method using ID-SSMS was developed for determining the mercury content of Orchard Leaves, Standard Reference Material 1571. Since we intend to detail the method in a future publication, only a brief description of the method is given here. A number of experiments were made with the apparatus shown in Figure 28, which is similar in design to that described for wet-oxidizing organic matter [45]. In our procedure, an additional function of the apparatus is to promote equilibrium between the natural mercury in the sample and the enriched isotope spike, as will be described.

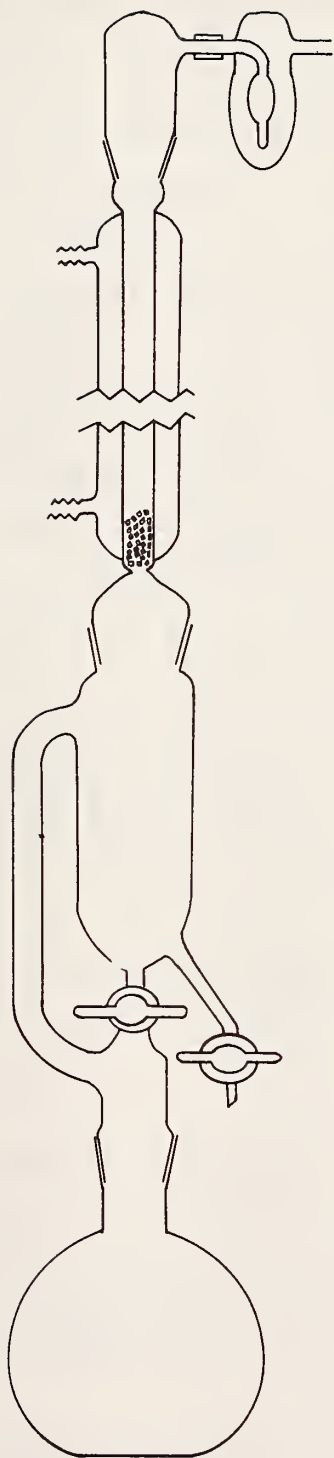


Figure 28. Apparatus for digestion of organic samples and equilibration of mercury.

Samples were weighed into flasks, spiked with known volumes of solution containing an enriched isotope of mercury, and heated with nitric acid after assembling the apparatus. Perchloric and nitric acids were then added through the condenser and heated. To completely oxidize the organic material, the stopcock to the chamber was closed so that nitric acid could distill and collect in the chamber, thus increasing the concentration of perchloric acid in the flask. Because some of the mercury accompanies the distillate, the stopcock was opened, returning the distillate to the flask, thus equilibrating the mercury. After this step, loss of mercury does not invalidate the results. To concentrate the isotopically equilibrated mercury for electrodeposition onto gold-wire cathodes, the chamber and bubbler were removed and the acids distilled through the condenser from which water had been removed. After the electrolysis, the analysis was completed by sparking the wires in the mass spectrograph, measuring the isotopic ratios, and calculating the concentrations from the general isotope dilution equation. The results obtained agreed with those by activation analysis and atomic absorption spectroscopy, leading to a proposed certified value of 0.155 ± 0.015 $\mu\text{g/g}$.

These activities have been conducted as a joint investigation with Dr. Paul J. Paulsen of the Analytical Mass Spectrometry Section.

R. Alvarez

6. LIST OF PERSONNEL AND ACTIVITIES

A. Personnel

Spectrochemical Analysis Section

Bourdon F. Scribner, Chief (Promoted 1/71 to Deputy Division Chief)
Kurt F. J. Heinrich, Acting Chief (as of 1/71)
Stanley D. Rasberry, Acting Assistant Chief (as of 1/71)
Karen L. Loraski, Secretary
Donald C. Reid (Cooperative student program 1971)
Shelia M. Cregger (Youth summer program 1971)
Carolyn Perry (Youth summer program 1970)
Mary Simms (Youth summer program 1970)

Group I. Electron Probe Microanalysis

Kurt F. J. Heinrich, Chemist
Robert L. Myklebust, Chemist
Charles E. Fiori, Electronics Technician
Donald L. Vieth (Extended leave for educational purposes)

Group II. X-Ray Fluorescence Spectrometry

Stanley D. Rasberry, Physicist
Jerome S. McKay, Jr., Laboratory Assistant

Group III. Optical Spectrometry

Joseph L. Weber, Jr., Physicist
Martha M. Darr, Chemist
Virginia C. Stewart, Chemist (Retired)
Doward M. Bouchette, Physical Science Technician (Retired)

Group IV. Enrichment Techniques

Robert Alvarez, Chemist

B. Publications

1. French, B. M., Walter, L. S., and Heinrich, K. F. J.
Quantitative Mineralogy of an Apollo 11 Lunar
Sample, Geochim. Cosmochim. Acta 1, 433-44 (1970).
2. Heinrich, K. F. J.
Present State of the Classical Theory of Quantitative
Electron Probe Microanalysis, NBS Tech. Note 521
(1970).
3. Ahearn, A. J.
Quantitative Analysis of Solids by Spark Source Mass
Spectrometry in Proceedings of International Con-
ference on Mass Spectroscopy, Kyoto, Japan, Sept. 8-13,
1969, 150-157 (1970).
4. Scribner, B. F. (Editor)
Activities of the NBS Spectrochemical Analysis Section
July 1969 to June 1970, NBS Tech. Note 542 (1970).
5. Yakowitz, H., Fiori, C. E., and Michaelis, R. E.
Homogeneity Characterization of Fe-3Si Alloy, Nat.
Bur. Stand. (U.S.), Spec. Publ. 260-22, 22 pages
(1971).
6. Hicho, G. E., Yakowitz, H., Rasberry, S. D., and
Michaelis, R. E.
A Standard Reference Material Containing Nominally
Four Percent Austenite, Nat. Bur. Stand. (U.S.),
Spec. Publ. 260-25, 14 pages (1971).
7. Hicho, G. E., Yakowitz, H., Rasberry, S. D., and
Michaelis, R. E.
A Standard Reference Material Containing Nominally
Four Percent Austenite in Advances in X-ray Analysis,
14, 78-91, Plenum Press, N. Y. (1971).
8. Heinrich, K. F. J., Myklebust, R. L., Rasberry, S. D.,
and Michaelis, R. E.
Evaluation of SRM's 481 and 482 Gold-Silver and Gold-
Copper Alloys for Microanalysis, Nat. Bur. Stand.
(U.S.), Spec. Publ. 260-28, 89 pages (1971).

C. Talks Given

1. Rasberry, S. D., "The Division Computer System," Division 310 Scientific Discussion, July 15, 1970.
2. Heinrich, K. F. J., "Uncertainties in Quantitative Electron Probe Microanalysis," Fifth National Conference on Electron Microprobe Analysis, Electron Probe Analysis Society of America, New York, New York, July 22, 1970.
3. Heinrich, K. F. J., "An Improved Target Current Amplifier for the Electron Microprobe and the Scanning Electron Microscope," Fifth National Conference on Electron Microprobe Analysis, Electron Probe Analysis Society of America, New York, New York, July 24, 1970.
4. Alvarez, R., "The Analysis of a New NBS Standard Reference Material of Orchard Leaves by Isotope Dilution and Spark Source Mass Spectrometry," The Chemical Institute of Canada, Alberta, Canada, Aug. 20, 1970.
5. Heinrich, K. F. J., "Electron Probe Microanalysis, Quantitative Evaluation of Measurements (Theoretical Aspects)," VI International Symposium on Microtechniques, Graz, Austria, Sept. 10, 1970.
6. Heinrich, K. F. J., "Simultaneous Display of Composition and Topography by Color Composites of Electron Probe Microanalyzer Scans," The Royal Microscopical Society Symposia on Microscopy, London, England, Sept. 14, 1970.
7. Rasberry, S. D., "X-ray Fluorescence and Optical Emission Analysis of Five New Special Iron and Steel Standard Reference Materials," Ninth National Meeting of the Society for Applied Spectroscopy, New Orleans, La., Oct. 5, 1970.
8. Alvarez, R., "Electrodeposition of Trace Elements on Mercury-Coated Electrodes and Their Determination by High-Voltage Spark Excitation," Ninth National Meeting of the Society for Applied Spectroscopy, New Orleans, La., Oct. 9, 1970.
9. Alvarez, R., "Trace Determinations by Isotope Dilution-Spark Source Mass Spectrometry," Division 310 Scientific Discussion, Oct. 14, 1970.
10. Heinrich, K. F. J., "Electron Probe Microanalysis," Wayne State University, Detroit, Mich., Nov., 1970.

11. Rasberry, S. D., "Quantitative X-ray Spectrography: Regression Methods," Eastern Analytical Symposium, New York, N. Y., Nov. 8, 1970.
12. Alvarez, R., "The Determination of Problem Elements in New NBS Standard Reference Materials by Isotope Dilution, Spark Source Mass Spectrometry," Middle Atlantic Regional Meeting of the American Chemical Society, Baltimore, Md., Feb. 4, 1971.
13. Heinrich, K. F. J., "Electron Probe Microanalysis and Its Geochemical Applications," Department of Chemistry, University of Maryland, College Park, Md., Feb. 5, 1971.
14. Heinrich, K. F. J., "Electron Probe Microanalysis and Its Geochemical Applications," Division 310 Scientific Discussion, Feb. 10, 1971.
15. Rasberry, S. D., "Computers in Spectrochemical Analysis - The Software Byte," Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 3, 1971.
16. Alvarez, R., "The Characterization of an NBS Botanical Standard Reference Material for Environmental Lead and Nutrient Element Monitoring," Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 4, 1971.
17. Heinrich, K. F. J., "The Analysis of Trace Constituents with the Electron Probe Microanalyzer," 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 30, 1971.
18. Rasberry, S. D., "Recent Developments in X-ray Fluorescence Spectroscopy," Division 310 Scientific Discussion, April 21, 1971.
19. Alvarez, R., "Chemical Preconcentration Techniques for Analyzing NBS Standard Reference Materials by Optical Emission Spectroscopy," "Metrochem '71," American Chemical Society, San Juan, Puerto Rico, May 2, 1971.
20. Alvarez, R., "Simultaneous Determination of Cu, Ag, Zr, Se, Te, Ce, and Nd in Special Steel NBS SRM 1261 by Isotope Dilution, Spark Source Mass Spectrometry," "Metrochem '71," American Chemical Society, San Juan, Puerto Rico, May 2, 1971.
21. Darr, M. M., "Observations on Unique Sample Handling and Spectroscopic Techniques in Several Laboratories," Division 310 Scientific Discussion, May 5, 1971.

22. Heinrich, K. F. J., "Advances of Electron Probe Micro-analysis at the National Bureau of Standards," Canadian Probe Users' Group, London, Ontario, Canada, May 11, 1971.
23. Alvarez, R., "Scientific Activities in Puerto Rico," Division 310 Scientific Discussion, May 19, 1971.
24. Heinrich, K. F. J., "Scanning Electron Probe Analysis Techniques," Lehigh University, Bethlehem, Penn., June 22, 1971.
25. Heinrich, K. F. J., "Quantitative Electron Probe Analysis - Evaluation of Correction Procedures," Lehigh University, Bethlehem, Penn., June 23, 1971.

D. Committee Activities

B. F. Scribner

Member, ASTM Committee E-2 on Emission Spectroscopy
Member, ASTM Committee E-13 on Absorption Spectroscopy
Member, Advisory Board, Spectrochimica Acta, Atomic
Section
Member, Analytical Services Committee, NBS Analytical
Chemistry Division
Member, Washington Editorial Review Board, NBS
Member, David Richardson Medal Committee, Optical
Society of America
Member, Publications Committee, Society for Applied
Spectroscopy

K. F. J. Heinrich

Past President, Electron Probe Analysis Society of
America, 1970
Assistant Editor, Mikrochimica Acta

R. Alvarez

Member, ASTM Committee E-2 on Emission Spectroscopy
Member, Awards Committee, Baltimore-Washington Section,
SAS, 1970

J. L. Weber, Jr.

Member, ASTM Committee E-2 on Emission Spectroscopy,
Subcommittees IV, VII, and IX; Liaison to Committee B-7
Member, ASTM Committee B-7 on Light Metals and Alloys,
Cast and Wrought; Liaison to Committee E-2
Column Editor, Applied Spectroscopy
Alternate Delegate to Eastern Analytical Symposium from
Baltimore-Washington Section, SAS

S. D. Rasberry

Member, Laser Task Group, ASTM Committee E-2
Delegate, Baltimore-Washington Section, SAS, 1970-72
Member, Membership Education Committee, SAS, 1971
Member, Computer Evaluation Committee, NBS Analytical
Chemistry Division

M. M. Darr

Member, ASTM Committee E-2 on Emission Spectroscopy,
Subcommittee XII

R. L. Myklebust

Member, Yearbook Committee, Washington Section, ASM,
1970-72

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The cooperation of Dr. Gerald Sleater, of the Building Research Division, on initial studies for detecting lead in paint has been most helpful.

In the design and development of electronic instrumentation for spectrochemical analysis, the help of Louis Marzetta, Measurement Engineering Division, has been indispensable. Morris Schwartzmann of the same group has contributed to the repair of electronic equipment.

As in past years, excellent support has been received from the various NBS shops. Alex Fussinger of the Chemistry Division Contact Shop has been especially helpful in the fabrication of instrument parts without detailed drawings.

On numerous occasions, Herbert Carter and Eugene Deardorff, Office of Standard Reference Materials, have lent an extra measure of skill to the solution of difficult specimen preparation problems; James Izlar, of the same group, has given us needed laboratory assistance in times when our own Section was under-manned.

Mrs. Rosemary Maddock and her group have continued to give us much assistance in the planning of slides for talks and illustrations for publication.

Finally, but most important, Karen Loraski, our Section Secretary, has daily provided valuable assistance to members of the Section in a variety of activities, especially in the preparation and typing of complex manuscripts and reports.

This list of acknowledgments is clearly incomplete; we are appreciative for assistance and counsel by many of our friends within and outside of NBS.

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APPENDIX A

CERTIFICATES FOR NBS STANDARD REFERENCE
MATERIALS RECENTLY ISSUED

Certificate of Analysis

Standard Reference Material 1261

AISI 4340 Steel

This standard is in the form of disks 31 mm (1 1/4 in) in diameter and 19 mm (3/4 in) thick, generally for use in optical emission and x-ray spectrometric analysis.^a

Element	Percent, by weight
Carbon	0.38 ₂
Manganese66
Phosphorus015
Sulfur017
Silicon223
Copper042
Nickel	1.99
Chromium	0.69
Vanadium011
Molybdenum19
Cobalt030
Titanium02 ₀
Arsenic01 ₂
Tin01 ₁
Aluminum (total)02 ₁
Niobium02 ₂
Zirconium008
Antimony004 ₂
Cerium001 ₃

^aThis material also is available in the form of chips, SRM 361, for use in chemical methods of analysis; rods, SRM 1095, 6.4 mm (1/4 in) in diameter and 102 mm (4 in) long for the determination of gases in metals by vacuum fusion and neutron activation methods of analysis; and rods, SRM 661, 3.2 mm (1/8 in) in diameter and 51 mm (2 in) long for application in microchemical methods of analysis such as electron probe microanalysis, spark source mass spectrometric analysis, and laser probe analysis.

PROVISIONAL CERTIFICATION: The value listed for a certified element is the present best estimate of the true value based on the results of the cooperative analytical program. The value listed is not expected to deviate from the true value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5 . Based on the results of homogeneity testing, maximum variations within and among samples are estimated less than the accuracy figures given above.

The overall direction and coordination of the technical measurements at NBS leading to certification were performed under the direction of O. Menis, B. F. Scribner, J. I. Shultz, and J. L. Weber, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D. C. 20234
July 26, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

(over)

PLANNING, PREPARATION, TESTING, ANALYSIS: This standard is one of five replacements for the original eight 1100 series iron and steel SRMs. Material from the same melt is available in a variety of forms to serve in checking methods of analysis and in calibrating instrumental techniques.

The material for this standard was vacuum melted and cast at the Carpenter Technology Corporation, Reading, Pennsylvania, under a contract with the National Bureau of Standards. The contract was made possible by a grant from the American Iron and Steel Institute.

The ingots were processed by Carpenter Technology Corporation to provide material of the highest possible homogeneity. Following acceptance of the composition based on NBS analyses, selected portions of the ingot material were extensively tested for homogeneity at NBS by D. M. Bouchette, S. D. Rasberry, and J. L. Weber, Jr. Only that material meeting a critical evaluation was processed to the final sizes.

Chemical analyses for certification generally were made on composite samples representative of each final shape and size; for certain elements, however, and based on previous experience, only one composite sample was analyzed with the results applied to the other forms of the material.

Cooperative analyses for certification were performed in the analytical laboratories of Bethlehem Steel Corporation, Sparrows Point Plant, Maryland, R. H. Rouse; Carpenter Technology Corporation, Research and Development Center, Reading, Pennsylvania, E. J. Cramer; The Timken Roller Bearing Company, Steel & Tube Division, Canton, Ohio, R. G. Cover; United States Steel Corporation, Applied Research Laboratory, Monroeville, Pennsylvania, L. Melnick, and Gary Steel Works, Gary, Indiana, E. H. Shipley.

Analyses were performed in the Analytical Chemistry Division of the National Bureau of Standards by the following: R. Alvarez, J. R. Baldwin, D. A. Becker, E. L. Garner, T. E. Gills, E. J. Maienthal, C. W. Mueller, P. J. Paulsen, K. M. Sappenfield, B. A. Thompson, S. A. Wicks, and J. Wing.

ADDITIONAL INFORMATION ON THE COMPOSITION: Provisional certification is made only for the elements indicated. The five replacements, however, contain a graded series for 40 elements and information on the elements not initially certified may be of importance in the use of the material. Although these are not certified, values are presented in the following table for the remaining elements. (Some may be certified at a later date.)

Value from a single laboratory

<u>Element</u>	<u>Percent, by weight</u>
Tungsten	(0.011)
Tantalum	(.021)
Lead	(<.0001)
Bismuth	(.0004)
Silver	(.0004)
Selenium	(.004)
Tellurium	(.0006)
Lanthanum	(.0004)
Neodymium	(.0003)
Nitrogen	(.0037)
Iron (by difference)	(95.6)

Approximate value from heat analysis

Boron	(0.0005)
Calcium	(.0001)
Magnesium	(.0002)
Zinc	(.0005)
Praseodymium	(.0002)
Germanium	(.006)
Oxygen	(.001)
Hydrogen	(<.0005)
Gold	(<.00005)
Hafnium	(.0002)

Certificate of Analysis

Standard Reference Material 1262

AISI 94B17 Steel (Modified)

This standard is in the form of disks 31 mm (1 1/4 in) in diameter and 19 mm (3/4 in) thick, generally for use in optical emission and x-ray spectrometric analysis.^a

<u>Element</u>	<u>Percent, by weight</u>
Carbon	0.16 ₀
Manganese	1.04
Phosphorus	0.042
Sulfur038
Silicon39
Copper50
Nickel59
Chromium30
Vanadium04 ₁
Molybdenum06 ₂
Cobalt30
Antimony012

^aThis material also is available in the form of chips, SRM 362, for use in chemical methods of analysis; rods, SRM 1096, 6.4 mm (1/4 in) in diameter and 102 mm (4 in) long for the determination of gases in metals by vacuum fusion and neutron activation methods of analysis; and rods, SRM 662, 3.2 mm (1/8 in) in diameter and 51 mm (2 in) long for application in microchemical methods of analysis such as electron probe microanalysis, spark source mass spectrometric analysis, and laser probe analysis.

PROVISIONAL CERTIFICATION. The value listed for a certified element is the present best estimate of the true value based on the results of the cooperative analytical program. The value listed is not expected to deviate from the true value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5 . Based on the results of homogeneity testing, maximum variations within and among samples are estimated less than the accuracy figures given above.

The overall direction and coordination of the technical measurements at NBS leading to certification were performed under the direction of O. Menis, B. F. Scribner, J. I. Shultz, and J. L. Weber, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D. C. 20234
July 27, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

PLANNING, PREPARATION, TESTING, ANALYSIS: This standard is one of five replacements for the original eight 1100 series iron and steel SRMs. Material from the same melt is available in a variety of forms to serve in checking methods of analysis and in calibrating instrumental techniques.

The material for this standard was vacuum melted and cast at the Carpenter Technology Corporation, Reading, Pennsylvania, under a contract with the National Bureau of Standards. The contract was made possible by a grant from the American Iron and Steel Institute.

The ingots were processed by Carpenter Technology Corporation to provide material of the highest possible homogeneity. Following acceptance of the composition based on NBS analyses, selected portions of the ingot material were extensively tested for homogeneity at NBS by D. M. Bouchette, S. D. Rasberry, and J. L. Weber, Jr. Only that material meeting a critical evaluation was processed to the final sizes.

Chemical analyses for certification generally were made on composite samples representative of each final shape and size; for certain elements, however, and based on previous experience, only one composite sample was analyzed with the results applied to the other forms of the material.

Cooperative analyses for certification were performed in the analytical laboratories of Allegheny Ludlum Steel Corporation Research Center, Brackenridge, Pennsylvania, R. B. Fricioni; Inland Steel Company, East Chicago, Indiana, R. W. Bley and J. E. Joyce; Republic Steel Corporation, Canton, Ohio, R. W. Jones; and The Youngstown Sheet and Tube Company, Youngstown, Ohio, L. E. Chalker.

Analyses were performed in the Analytical Chemistry Division of the National Bureau of Standards by the following: J. R. Baldwin, R. K. Bell, R. W. Burke, T. E. Gills, L. T. McClendon, B. A. Thompson, and S. A. Wicks.

ADDITIONAL INFORMATION ON THE COMPOSITION: Provisional certification is made only for the elements indicated. The five replacements, however, contain a graded series for 40 elements and information on the elements not initially certified may be of importance in the use of the material. Although these are not certified, values are presented in the following table for the remaining elements. (Some may be certified at a later date)

Value from a single laboratory

<u>Element</u>	<u>Percent, by weight</u>
Titanium	(0.083)
Arsenic	(.094)
Tin	(.016)
Aluminum (soluble)	(.086)
Boron	(.0025)
Lanthanum	(.0004)
Nitrogen	(.0041)
Oxygen	(.001)
Gold	(<.00006)
Iron (by difference)	(95.3)

Approximate value from heat analysis

Tungsten	(0.20)
Niobium	(.28)
Tantalum	(.20)
Lead	(.0006)
Zirconium	(.21)
Bismuth	(.006)
Silver	(.0009)
Calcium	(.0003)
Magnesium	(.0007)
Selenium	(.001)
Tellurium	(.001)
Zinc	(.001)
Cerium	(.002)
Praseodymium	(.0003)
Neodymium	(.0005)
Germanium	(.002)
Hydrogen	(<.0005)
Hafnium	(.006)

Certificate of Analysis

Standard Reference Material 1263

Cr-V Steel (Modified)

This standard is in the form of disks 31 mm (1 1/4 in) in diameter and 19 mm (3/4 in) thick, generally for use in optical emission and x-ray spectrometric analysis.^a

<u>Element</u>	<u>Percent, by weight</u>
Carbon	0.62
Manganese	1.50
Phosphorus	0.02 ₉
Sulfur008
Silicon74
Copper09 ₈
Nickel32
Chromium	1.31
Vanadium31
Molybdenum030
Cobalt04 ₈
Antimony001 ₆

^aThis material also is available in the form of chips SRM 308, for use in chemical methods of analysis; and will be available in the form of rods, SRM 1097, 6.4 mm (1/4 in) in diameter and 102 mm (4 in) long for the determination of gases in metals by vacuum fusion and neutron activation methods of analysis; and rods, SRM 663, 3.2 mm (1/8 in) in diameter and 51 mm (2 in) long for application in microchemical methods of analysis such as electron probe microanalysis, spark source mass spectrometric analysis, and laser probe analysis.

PROVISIONAL CERTIFICATION. The value listed for a certified element is the present best estimate of the true value based on the results of the cooperative analytical program. The value listed is not expected to deviate from the true value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5 . Based on the results of homogeneity testing, maximum variations within and among samples are estimated less than the accuracy figures given above.

The overall direction and coordination of the technical measurements at NBS leading to the certification were performed under the direction of O. Menis, B. F. Scribner, J. I. Shultz, and J. L. Weber, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D. C. 20234
October 2, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

(over)

PLANNING, PREPARATION, TESTING, ANALYSIS: This standard is one of five replacements for the original eight 1100 series iron and steel SRMs. Material from the same melt is available in a variety of forms to serve in checking methods of analysis and in calibrating instrumental techniques.

The material for this standard was vacuum melted and cast at the Carpenter Technology Corporation, Reading, Pennsylvania, under a contract with the National Bureau of Standards. The contract was made possible by a grant from the American Iron and Steel Institute.

The ingots were processed by Carpenter Technology Corporation to provide material of the highest possible homogeneity. Following acceptance of the composition based on NBS analyses, selected portions of the ingot material were extensively tested for homogeneity at NBS by D. M. Bouchette, S. D. Rasberry, and J. L. Weber, Jr. Only that material meeting a critical evaluation was processed to the final sizes.

Chemical analyses for certification generally were made on composite samples representative of each final shape and size; for certain elements, however, and based on previous experience, only one composite sample was analyzed with the results applied to the other forms of the material.

Cooperative analyses for certification were performed in the analytical laboratories of Climax Molybdenum Company of Michigan, Ann Arbor, Michigan, J. W. Mann and H. E. Trapp; Midvale-Heppenstall Co., Nicetown, Philadelphia, Pennsylvania, W. L. MacBride; Standard Steel Co., Burnham, Pennsylvania, J. Metzgar; and The Steel Company of Canada, Hamilton, Ontario, Canada, O. P. Bhargava.

Analyses were performed in the Analytical Chemistry Division of the National Bureau of Standards by the following: R. K. Bell, R. W. Burke, T. E. Gills, E. J. Maienthal, L. T. McClendon, T. C. Rains, T. A. Rush, B. A. Thompson, and S. A. Wicks.

ADDITIONAL INFORMATION ON THE COMPOSITION: Provisional certification is made only for the elements indicated. The five replacements, however, contain a graded series for 40 elements and information on the elements not initially certified may be of importance in the use of the material. Although these are not certified, values are presented in the following table for the remaining elements. (Some may be certified at a later date.)

Value from a single laboratory

<u>Element</u>	<u>Percent, by weight</u>
Tungsten	(0.050)
Arsenic	(.010)
Lead	(.0016)
Bismuth	(.0008)
Silver	(.0038)
Calcium	(<.0001)
Magnesium	(.0005)
Tellurium	(.0022)
Zinc	(.0004)
Lanthanum	(.0006)
Gold	(.0005)
Iron (by difference).	(94.4)

Approximate value from heat analysis

Titanium	(0.06)
Tin	(.094)
Aluminum	(.25)
Niobium	(.049)
Tantalum	(.04)
Boron	(.0010)
Zirconium	(.048)
Selenium	(.0001)
Cerium	(.002)
Praseodymium	(.0005)
Nitrogen	(.0042)
Germanium	(.010)
Oxygen	(.0006)
Hydrogen	(<.0005)
Hafnium	(.0015)

Certificate of Analysis

Standard Reference Material 1264

High-Carbon Steel (Modified)

This standard is in the form of disks 31 mm (1 1/4 in) in diameter and 19 mm (3/4 in) thick, generally for use in optical emission and x-ray spectrometric analysis.^a

<u>Element</u>	<u>Percent, by weight</u>
Carbon	0.87
Manganese25 ₅
Phosphorus01 ₈
Sulfur02 ₉
Silicon06 ₅
Copper24 ₉
Nickel13 ₉
Chromium06 ₃
Vanadium10 ₅
Molybdenum49
Cobalt14
Lead01 ₉

^aThis material also will be available in the form of chips, SRM 664, for use in chemical methods of analysis; rods, SRM 1098, 6.4 mm (1/4 in) in diameter and 102 mm (4 in) long for the determination of gases in metals by vacuum fusion and neutron activation methods of analysis; and rods, SRM 664, 3.2 mm (1/8 in) in diameter and 51 mm (2 in) long for application in microchemical methods of analysis such as electron probe microanalysis, spark source mass spectrometric analysis, and laser probe analysis.

PROVISIONAL CERTIFICATION The value listed for a certified element is the present best estimate of the true value based on the results of the analytical program. The value listed is not expected to deviate from the true value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5 . Based on the results of homogeneity testing, maximum variations within and among samples are estimated less than the accuracy figures given above.

The overall direction and coordination of the technical measurements at NBS leading to the certification were performed under the direction of O. Menis, B. F. Scribner, J. I. Shultz, and J. L. Weber, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D. C. 20234
January 20, 1971

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

PLANNING, PREPARATION, TESTING, ANALYSIS: This standard is one of five replacements for the original eight 1100 series iron and steel SRMs. Material from the same melt is available in a variety of forms to serve in checking methods of analysis and in calibrating instrumental techniques.

The material for this standard was vacuum melted and cast at the Carpenter Technology Corporation, Reading, Pennsylvania, under a contract with the National Bureau of Standards. The contract was made possible by a grant from the American Iron and Steel Institute.

The ingots were processed by Carpenter Technology Corporation to provide material of the highest possible homogeneity. Following acceptance of the composition based on NBS analyses, selected portions of the ingot material were extensively tested for homogeneity at NBS by D. M. Bouchette, S. D. Rasberry, and J. L. Weber, Jr. Only that material meeting a critical evaluation was processed to the final sizes.

Chemical analyses for certification generally were made on composite samples representative of each final shape and size; for certain elements, however, and based on previous experience, only one composite sample was analyzed with the results applied to the other forms of the material.

Analyses were performed in the Analytical Chemistry Division of the National Bureau of Standards by the following: R. K. Bell, T. E. Gills, E. J. Maienthal, S. D. Rasberry, B. A. Thompson, and S. A. Wicks.

CAUTION: This standard has been found generally satisfactory for application in x-ray spectrometric analysis with the analytical points fitting on curves established by use of the 1100 Series. However, in preliminary application testing for optical emission spectrometric analysis with conventional air-spark excitation, some biases were observed relative to curves from the 1100 series — particularly for the carbide-forming elements. This may be due to metallurgical structure differences in this standard (more carbides) or composition interferences (higher carbon, molybdenum, and titanium). In any event the user is cautioned in application of this standard to test its comparability with other available SRMs.

ADDITIONAL INFORMATION ON THE COMPOSITION: Provisional certification is made only for the elements indicated. The five replacements, however, contain a graded series for 40 elements and information on the elements not initially certified may be of importance in the use of the material. Although these are not certified, values are presented in the following table for the remaining elements. (Some may be certified at a later date.)

Value from a single laboratory

<u>Element</u>	<u>Percent, by weight</u>
Tungsten	(0.10)
Titanium	(.24)
Arsenic	(.057)
Niobium	(.157)
Tantalum	(.11)
Zirconium	(.070)
Lanthanum	(.00007)
Gold	(.00007)
Iron (by difference)	(96.7)

Approximate value from heat analysis

Tin	(0.005)
Aluminum	(.014)
Boron	(.014)
Antimony	(.025)
Bismuth	(.002)
Silver	(.00005)
Calcium	(.00005)
Magnesium	(.00005)
Selenium	(.0003)
Tellurium	(.0002)
Zinc	(.0005)
Cerium	(.0005)
Praseodymium	(.0001)
Nitrogen	(.003)
Germanium	(.003)
Oxygen	(.0017)
Hydrogen	(<.0005)
Hafnium	(.005)
Neodymium	(.0002)

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 1265

Electrolytic Iron

This standard is in the form of disks 32 mm (1 1/4 in) in diameter and 19 mm (3/4 in) thick, generally for use in optical emission and x-ray spectrometric analysis.^a

<u>Element</u>	<u>Percent, by weight</u>
Carbon	0.0067
Manganese0057
Phosphorus002 ₅
Sulfur0059
Silicon008 ₀
Copper0058
Nickel041
Chromium007 ₂
Vanadium0006
Molybdenum0050
Cobalt007 ₀
Titanium0006
Arsenic	(.0002) ^b
Aluminum (Total)	(.0007)
Boron00013
Lead00002
Iron (by difference)	99.9

^aThis material also is available in the form of chips, SRM 365, for use in chemical methods of analysis; rods, SRM 1099, 6.4 mm (1/4 in) in diameter and 102 mm (4 in) long for the determination of gases in metals by vacuum fusion and neutron activation methods of analyses; and rods, SRM 665, 3.2 mm (1/8 in) in diameter and 51 mm (2 in) long for application in microchemical methods of analysis such as electron probe microanalysis, spark source mass spectrometric analysis, and laser probe analysis.

^bValues in parenthesis are not certified since they are based on the results from a single laboratory.

CERTIFICATION: The value listed for a certified element is the best estimate of the true value based on the results of the cooperative analytical program. The value listed is not expected to deviate from the true value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5 . Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than the accuracy figures given above.

Washington, D. C. 20234
August 6, 1971

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

PLANNING, PREPARATION, TESTING, ANALYSIS: This standard is one of five replacements for the original eight 1100 series iron and steel SRM's. Material from the same melt is available in a variety of forms to serve in checking methods of analysis and in calibrating instrumental techniques.

The material for this standard was vacuum melted and cast at the Carpenter Technology Corporation, Reading, Pennsylvania, under a contract with the National Bureau of Standards. The contract was made possible by a grant from the American Iron and Steel Institute.

The ingots were processed by Carpenter Technology Corporation to provide material of the highest possible homogeneity. Following acceptance of the composition based on NBS analyses, selected portions of the ingot material were extensively tested for homogeneity at NBS by J. R. Baldwin, D. M. Bouchette, S. D. Rasberry, and J. L. Weber, Jr. Only that material meeting a critical evaluation was processed to the final sizes.

Chemical analyses for certification were made on composite samples representative of the accepted lot of material.

Cooperative analyses for certification were performed in the Research Laboratories of Armco Steel Corporation by R. L. LeRoy and J. F. Woodruff.

Analyses were performed in the Analytical Chemistry Division of the National Bureau of Standards by the following: R. Alvarez, J. R. Baldwin, E. Belkas, B. S. Carpenter, M. M. Darr, E. R. Deardorff, E. L. Garner, T. E. Gills, L. A. Machlan, E. J. Maienthal, L. J. Moore, C. W. Mueller, T. J. Murphy, P. J. Paulsen, K. M. Sappenfield, B. A. Thompson, and S. A. Wicks.

The overall direction and coordination of the technical measurements at NBS leading to certification were performed under the direction of O. Menis, B. F. Scribner, J. I. Shultz, and J. L. Weber, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

ADDITIONAL INFORMATION ON THE COMPOSITION: Certification is made only for the elements indicated. The five replacements, however, contain a graded series for 40 elements and information on the elements not initially certified may be of importance in the use of the material. Although these are not certified, upper limit values are presented in the following table for the remaining elements. (Some may be certified at a later date.)

Elements Detected (ppm by weight)

<u>Element</u>	<u>Upper Limit</u>	<u>(Estimated value)</u>	<u>Method</u>
W	< 1	(0.4)	Neutron activation
Sn	< 5	(2)	Spark source mass spectrometry
Nb	< 0.5	(<0.1)	Spark source mass spectrometry
Ag	< 0.2	(0.02)	Spark source mass spectrometry
Zn	< 3	(2)	Spark source mass spectrometry
N	<20	(~11)	Distillation-photometric
Ge	<50	(~14)	Spark source mass spectrometry
O	<70	(63)	Vacuum fusion
H	< 5	(1)	Vacuum fusion

Elements Sought But Not Detected (ppm by weight)

<u>Element</u>	<u>Upper Limit</u>	<u>Method</u>
Ta	<0.5	Neutron activation
Zr	<0.1	Spark source mass spectrometry
Sb	<0.5	Neutron activation
Bi	<0.1	Spark source mass spectrometry
Ca	<0.1	Atomic absorption
Mg	<0.2	Atomic absorption
Se	<0.1	Spark source mass spectrometry
Te	<0.1	Spark source mass spectrometry
Ce	<0.05	Spark source mass spectrometry
La	<0.05	Spark source mass spectrometry
Pr	<0.05	Spark source mass spectrometry
Au	<0.02	Neutron activation
Hf	<0.2	Spark source mass spectrometry
Nd	<0.05	Spark source mass spectrometry

Certificate of Analysis

Standard Reference Material 483

Fe-3Si Alloy Microprobe Standard^a

This standard is characterized for chemical homogeneity of iron and silicon at the micrometer level of spatial resolution and is satisfactory for use as a homogeneous material for electron probe microanalysis.

SRM	Silicon	Iron (by difference)
	Weight, percent	
483	3.22 ^b ± 0.02 ^c	96.7 – 96.8

^aSize: 3 mm × 3 mm × 0.28 mm thick. The material is from coarse-grained sheet stock having the so-called Goss orientation in which a [110] grain is parallel to the surface and [001] is the rolling direction. Each sample is supplied HF etched and ready for metallographic mounting and polishing.

^bDetermination of silicon involved 49 samples of SRM 483. SRM 125b, certified at 2.89 wt. % Si, was used as a control standard and 2.90 wt. % Si was found.

Method: One gram samples were dissolved in hydrochloric and nitric acids. A double dehydration of the silicon with perchloric acid was made with an intervening filtration. The weight of silicon present was determined from the loss resulting from treatment with hydrofluoric acid. Analyst – R. A. Paulson, NBS Analytical Chemistry Division.

^cStandard deviation of a single determination based on results obtained on SRM's 483 and 125b, but also including similar method error estimations from previous determinations.

HOMOGENEITY TESTING AND QUANTITATIVE ANALYSIS BY ELECTRON PROBE MICROANALYSIS

Homogeneity was checked by means of quantitative raster scanning in which a square matrix (1.1 mm × 1.1 mm) of individual points is analyzed by the microprobe. Each matrix represents 400 separate analyses. Six selected matrices were run for iron and silicon with three of these rerun. The coefficient of variation for both the iron and silicon is less than one percent. Analysts – H. Yakowitz, NBS Metallurgy Division, and C. E. Fiori, NBS Analytical Chemistry Division.

Quantitative microprobe analysis of this alloy gave a silicon content of 3.14 wt. % and an iron content of 96.9%. Analyst – H. Yakowitz, NBS Metallurgy Division.

Details of the microprobe testing and analyses, as well as the sample preparation, are given in NBS Special Publication 260-22, Standard Reference Materials: Homogeneity Characterization of Fe-3Si Alloy, H. Yakowitz, C. E. Fiori, and R. E. Michaelis, Feb. 1971.

The technical and support aspects involved in the preparation, certification, and issuance of this standard were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D. C. 20234
June 11, 1971

J. Paul Cali, Chief
Office of Standard Reference Materials

Certificate

Standard Reference Material 485

Austenite in Ferrite

This standard is provided for the calibration of x-ray diffraction equipment used in determining the amount of retained austenite in ferrous materials. X-ray diffraction procedures require accurate measurements of integrated intensity for a number of selected peaks; however, as the amount of retained austenite decreases, the accuracy of these measurements deteriorates. This nominally four percent austenite standard should serve the calibration needs at the low levels.

<u>SRM No.</u>	<u>Description</u>	<u>Austenite, percent</u>
485	Austenite in Ferrite	4 (Nominal) ^b

^a The austenite standard is available in disk form, 29.6 mm (1 3/16 in) in diameter by 2.5 mm (0.10 in) thick.

^b Only one face on each disk is certified; the opposite face is labeled with the determined austenite content to the nearest 0.1 percent. The certified value is believed accurate to ± 0.2 percent. **CAUTION:** Damage to the certified face renders the certification of that disk void.

The preparation of specimens, and the technical measurements leading to certification, were directed and coordinated by G. E. Hicho.

The technical and support aspects involved in the preparation, certification, and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D. C. 20234
July 30, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

(over)

SUPPLEMENTARY INFORMATION

The austenite content of this standard is directly related to the nickel content as a result of blending austenitic stainless steel powder (20.4% Ni) with ferritic stainless steel powder (<0.1% Ni). Therefore, accurate and rapid x-ray fluorescence analysis could be used for the determination of the nickel content, and hence the austenite content, of each sintered and pressed compact.

An x-ray fluorescence analytical curve relating Ni K α count rate to austenite content was established using five specially prepared compacts which were characterized by the following two methods:

1. Quantitative Television Microscopy: Eighty fields were observed on each of the five compacts containing 5, 10, 15, 20, and 25 percent austenite, respectively. Observation covered three different time intervals. (D. E. Harne and G. E. Hicho)

2. Electro-Mechanical Drum Scanner: Five fields were observed on each compact: the center, and four mid-points of the center and the radius at 45 degrees with the horizontal and vertical. (D. E. Harne, G. E. Hicho, and G. A. Moore)

The x-ray fluorescence curve established through the use of the compacts characterized by the above methods was found valid to within ± 0.2 percent of austenite. The certified value for each disk of SRM 485 is based on the results of three determinations of the Ni K α count rate converted to austenite content. (S. D. Rasberry and H. Yakowitz)

This standard has been established to provide a means for calibrating x-ray diffraction equipment. The SRM 485, in special cases, may be used as an x-ray fluorescence standard for determining the nickel content in nickel-iron or nickel-chromium-iron composites.

The powder for SRM 485 was prepared at the Federal Mogul Corporation, Detroit, Michigan, and the compacts were prepared at SKC/PM Engineering of Hawthorne, New Jersey.

Certificate of Analysis

Standard Reference Materials

1206-2, 1207-1, 1207-2, 1208-1, 1208-2

High-Temperature Alloys: René 41, Waspaloy, and Inco 718

These standards are in the form of solid sections primarily for application in x-ray spectrometric analysis although they also may be useful in optical emission spectrometric analysis.

	René 41	Waspaloy		Inco 718	
	1206-2	1207-1	1207-2	1208-1	1208-2
Carbon	0.21 ₇	0.043	0.083	0.046	0.022
Manganese	.030	.34	.29 ₅	.38 ₅	.23 ₀
Phosphorus	(.004) ^a	.005	.005	.003	.003
Sulfur	.006	.009	.009	.01 ₁	.007
Silicon	.21 ₆	.47 ₂	.61 ₅	.43 ₄	.08 ₃
Copper	.040	.026	.033	.14 ₇	.077
Nickel	53.3	56.1	55.7	51.9	51.5
Chromium	19.17	18.88	19.4 ₄	17.5	17.4
Molybdenum	10.3 ₀	4.50	4.34	3.2 ₄	3.13
Titanium	2.9 ₄	3.09	2.54	0.46	(0.8 ₅)
Aluminum	1.7 ₄	1.26	1.3 ₁	(.15)	(.8 ₅)
Cobalt	11.5 ₅	13.0 ₅	13.5 ₀	.82	.76
Niobium	--	--	--	5.3 ₈	4.9 ₈
Iron	0.46	2.22	2.09	19.2	19.8
Tantalum	--	--	--	(0.012)	(0.012)

^aValues in parenthesis are not certified but are provided for additional information on the composition.

SIZE AND METALLURGICAL CONDITION: Samples are approximately 31 mm (1 1/4 in) square and 19 mm (3/4 in) thick; they were chill-cast by a rapid unidirectional solidification technique.

CERTIFIED PORTION: The certified portion for each sample is that extending upward 8 mm (5/16 in) from the chill-cast or test surface (the largest surface opposite the numbered surface). This portion only was analyzed in the cooperative program for certification.

PROVISIONAL CERTIFICATION: The value listed for a certified element is the present best estimate of the true value based on the results of the cooperative analytical program. The value listed is not expected to deviate from the true value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5 . Based on the results of homogeneity testing, maximum variations within and among samples are estimated less than the accuracy figures given above.

Note 1. The total for elements determined in SRMs 1206-2, 1207-1, and 1207-2 is 100.0 percent ± 0.05 ; for SRMs 1208-1 and 1208-2 the total is 99.7 percent ± 0.05 , suggesting the presence of one or more additional elements not yet sought nor determined.

Note 2: Metallographic examination of the material from SRM 1206-1 revealed considerable porosity precluding certification at this time.

Washington, D. C. 20234
November 6, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

(over)

PREPARATION, TESTING, ANALYSIS: The material for the standards was melted and cast at the American Cast Iron Pipe Company, Birmingham, Alabama, with use of the NBS chill-cast mold assembly. This procedure for the preparation and homogeneity testing was similar to that described in NBS Misc. Publ. 260-1, Standard Reference Materials: Preparation of NBS White Cast Iron Spectrochemical Standards, Robert E. Michaelis and LeRoy L. Wyman, June 19, 1964.

Homogeneity testing was performed at NBS by D. M. Bouchette and was found to be satisfactory for the elements certified.

Cooperative analyses for certification were performed in the analytical laboratories of Cameron Iron Works, Inc., Houston, Texas, R. A. Clarke; Carpenter Technology Corporation, Research and Development Center, Reading, Pennsylvania, E. J. Cramer; Ladish Co., Cudahy, Wisconsin, F. J. Kohls, J. Rafalski, and J. Szmania; and Cyclops Corporation, Universal-Cyclops Specialty Steel Division, Bridgeville, Pennsylvania, R. C. Host.

Analyses were performed in the Analytical Chemistry Division of the National Bureau of Standards by R. K. Bell, and S. A. Wicks.

Technical measurements performed at NBS for certification were coordinated by J. I. Shultz and J. L. Weber, Jr. under the chairmanship of B. F. Scribner.

The technical and support aspects involved in the preparation, certification, and issuance of these standard reference materials were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

CAUTIONS:

1. Determinations made on other than the chill-cast or test surface are not recommended because of the unidirectional solidification structure.
2. These chill-cast standards are designed for calibration in the analysis of samples prepared in the same manner; samples prepared by other casting techniques may result in considerable bias.
3. Because the samples exhibit some change with respect to the solidification structure, both among standards and from bottom to top of the certified portion of the samples, the surface preparation for x-ray spectrometric analysis may be critical. (A metallographic polishing technique is recommended.)
4. Because of the poor heat conductivity of the high-temperature alloys, difference in volatility rates for certain elements in emission spectrometric analysis may occur depending on the location of the burn and the source parameters.

Certificate of Analysis

STANDARD REFERENCE MATERIAL 1134

High-Silicon Steel

SIZE AND METALLURGICAL CONDITION: Samples are 1 1/4 in (31.8 mm) in diameter and 3/4 in (19.1 mm) thick, and are issued in the annealed condition. This material also is available in chip form as SRM 125b, primarily for application in chemical methods of analysis.

ANALYSTS	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	Sn	Al
	Combustion-Gravimetric	Peroxydisulfate-Arsenite	Molybdenum-Blue Photometric	Combustion-Iodate Titration	Perchloric Acid Dehydration	Photometric	Photometric	Photometric	Photometric		
1	0.024	0.278 ^a	0.029	0.008 ^b	2.89 ^c	$\left. \begin{matrix} 0.072^d \\ .071^e \end{matrix} \right\}$	0.039	0.016 ^f	0.009 ^f	0.003 ^g	0.332 ^h
2	.028 ⁱ	.276	.028	.010	2.89 ^c	.067 ^j	.036	$\left. \begin{matrix} .019^k \\ .022^l \end{matrix} \right\}$.008 ^m	.004 ⁿ	.329 ^o
3	.025 ⁱ	.277 ^p	.027 ^q	.008	2.88	.072 ^d	.039	.019 ^l	.008	.003 ⁿ	.326 ^r
Average	0.026	0.277	0.028	0.009	2.89	0.070	0.038	0.019	0.008	0.003	0.329

^a Potentiometric titration.

^b 1-g sample burned in oxygen at 1450 °C and sulfur dioxide absorbed in starch-iodide solution. Iodine is liberated from iodide by titration, during the combustion, with standard KIO₃ solution.

^c Double dehydration with intervening filtration.

^d Diethyldithiocarbamate spectrophotometric method.

^e Isotope dilution mass spectrometric method.

^f Activation analysis.

^g Sulfide-iodine method. See BS J. Res 8, 309 (1932) RP415.

^h Flame emission spectrometry.

ⁱ Thermal conductivity method.

^j Neocuproine spectrophotometric method.

^k Chromium oxidized with peroxydisulfate, titration with KMnO₄.

^l Diphenylcarbazide spectrophotometric method.

^m Thiocyanate-ethyleneglycol molybdenum complex extracted with monobutyl ether and determined spectrophotometrically.

ⁿ Polarographic method.

^o Aluminum precipitated as phosphate, ignited and weighed as AlPO₄.

^p Periodate spectrophotometric method.

^q Ammonium phosphomolybdate extracted with isobutyl alcohol reduced to molybdenum-blue, and phosphorus determined spectrophotometrically.

^r Ether, mercury-cathode, cupferron, chrome-azurol-S spectrophotometric method.

Washington, D. C. 20234
April 30, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

(over)

PLANNING, PREPARATION, TESTING, ANALYSIS: For many metal SRMs it is desirable to provide the material both in the form of chips primarily for chemical analysis and solids primarily for optical emission and x-ray spectrometric methods of analysis. Prior to the preparation of the renewal SRM 125b (chip form) plans were made also to provide this material as SRM 1134 (solid form).

The material for these standards was prepared by the Armco Steel Corporation. A single ingot was pressed to a slab having one dimension of the cross section four times that of the other dimension. After cropping top and bottom, the slab was cut lengthwise and the center section, corresponding to about one-fourth of the original ingot, was discarded. About half of the slab section material corresponding to the top part of the original ingot was rolled to 5-in diameter rounds and these rounds were subsequently chipped at NBS to form SRM 125b. The remaining slab sections were hot rolled to oversized rods and centerless ground to final rod size, 1 1/4 in (31.8 mm) in diameter.

Extensive homogeneity testing was performed at NBS and included metallographic studies by R. F. Brady, optical emission spectrometric analysis by D. M. Bouchette and J. L. Weber, Jr., x-ray spectrometric analysis by S. D. Rasberry and J. McKay, and chemical analysis by J. R. Baldwin and S. A. Wicks. The testing revealed the material to be of high homogeneity.

Chemical analyses were made on a composite chip sample for SRM 125b and on millings cut from the full cross section of the SRM 1134 material. The laboratories and analysts cooperating in the analytical program for certification are as follows:

1. J. R. Baldwin, S. A. Wicks, B. B. Bendigo, E. R. Deardorff, T. A. Rush, T. C. Rains, B. A. Thompson, T. J. Murphy, and E. L. Garner, Analytical Chemistry Division, Institute for Materials Research, National Bureau of Standards.
2. L. M. Melnick, W. R. Bandi, H. S. Karp, J. L. Lutz, R. W. Lewis, J. B. Ferons, and H. M. Lewis, Applied Research Laboratory, United States Steel Corporation, Monroeville, Pennsylvania.
3. M. Dannis and R. L. LeRoy, Armco Steel Corporation, Middletown, Ohio.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanships of O. Menis and J. I. Shultz.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Certificate of Analysis

Standard Reference Material 1623

Sulfur in Residual Fuel Oil

W. P. Schmidt and R. A. Paulson

Sulfur Content 0.268 ± 0.004 weight percent

This standard reference material is an analytical standard for determining sulfur in residual fuel oil. It is a commercially available fuel oil having the following inspection properties that are supplied for identification only: gravity, 27.0 °API; flash point (Pensky-Martens), 170 °F; viscosity (kinematic), 5.8 centistokes; pour point, 47 °F; and carbon residue (on 10 percent bottoms), 0.31 percent. The following analytical data are not certified, but are reported for information only: carbon, 87.4 percent; hydrogen, 12.0 percent; water, not detected (<0.1 percent); sediment, not detected (<0.01 percent); ash, not detected (<0.005 percent); and vanadium 3 ± 1 ng/g.

Sulfur was determined gravimetrically as barium sulfate after combustion in a Parr Oxygen Bomb using 1-g samples. The method is similar to ASTM Method D-129. It differs only in that any iron present is removed with ammonium hydroxide before the precipitation of the sulfur as barium sulfate. The uncertainty shown represents the 95-percent confidence limit of the mean based on 12 determinations and allowances for known sources of possible error.

The material was supplied by the Esso Research and Engineering Company of Linden, New Jersey. Vanadium was determined by T. E. Gills, using non-destructive neutron activation analysis.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of J. K. Taylor.

The technical and support aspects involved in the preparation, certification, and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by T. W. Mears.

Washington, D. C. 20234
April 7, 1971

J. Paul Cali, Chief
Office of Standard Reference Materials

Certificate of Analysis

Standard Reference Material 1624

Sulfur in Distillate Fuel Oil

W. P. Schmidt and R. A. Paulson

Sulfur Content 0.211 ± 0.004 weight percent

This standard reference material is an analytical standard for determining sulfur in distillate fuel oil. It is a commercially available oil having the following inspection properties that are supplied for identification only: gravity, 33.8 °API; flash point (Pensky-Martens), 138 °F; viscosity (kinematic), 2.7 centistokes; pour point, -16 °F; carbon residue (on 10 percent bottoms), 0.15 percent. The following analytical data are not certified, but are reported for information only: carbon, 86.6 percent; hydrogen, 12.5 percent; water, not detected (<0.1 percent); sediment, not detected (<0.01 percent); ash, not detected (<0.005 percent); vanadium, 14 ± 1 ng/g.

Sulfur was determined gravimetrically as barium sulfate after combustion in a Parr Oxygen Bomb using 1-g samples. The method is similar to ASTM Method D-129. It differs only in that any iron present is removed with ammonium hydroxide before the precipitation of the sulfur as barium sulfate. The uncertainty shown represents the 95-percent confidence limit of the mean based on 12 determinations and allowances for known sources of possible error.

The material was supplied by the Esso Research and Engineering Company of Linden, New Jersey. Vanadium was determined by T. E. Gills, using non-destructive neutron activation analysis.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of J. K. Taylor.

The technical and support aspects involved in the preparation, certification, and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by T. W. Mears.

Washington, D. C. 20234
April 7, 1971

J. Paul Cali, Chief
Office of Standard Reference Materials

Certificate of Analysis

Standard Reference Material 654a

Titanium Alloy, 6Al-4V

This standard is in the form of disks 31 mm (1 1/4 in) in diameter and 6.4 mm (1/4 in) thick, primarily for application in x-ray spectrometric analysis.^a

Element	Percent, by weight
Al	6.3 ₄
V	3.9 ₅
Fe	(0.20) ^b
Cr	(.20)
Mn	(<.1)
Mo	(<.05)

^aThis standard also may be useful in optical emission spectrometric analysis. Because the standard is thin, bonding it to a more massive backing will permit a greater efficiency in consumption of the material. See ASTM Designation E401-70, Recommended Practice for Bonding Thin Spectrochemical Samples and Standards to a Greater Mass of Material.

^bValues in parenthesis are not certified but are given as additional information on the composition.

PROVISIONAL CERTIFICATION: The value listed for a certified element is the present best estimate of the true value based on the results of two independent methods of analysis. Deviation of the true value by more than ± 5 in the last subscript figure is not expected. Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than the accuracy figure given above.

PLANNING, PREPARATION, TESTING, ANALYSIS: This standard was prepared, in part, to serve in round-robin testing and in calibration of an ASTM method (E02 SM8-20).

The material for the standard was provided in wrought form by the Research Center, Armco Steel Corporation, Middletown, Ohio.

Homogeneity testing and analyses for certification were performed in the Analytical Chemistry Division of the National Bureau of Standards by S. D. Rasberry and J. L. Weber, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this standard were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D. C. 20234
March 22, 1971

J. Paul Cali, Chief
Office of Standard Reference Materials

Certificate of Analysis

Standard Reference Material 917

D-Glucose

B. Coxon and R. Schaffer

This standard reference material is certified as a chemical of known purity. It is intended primarily for use in the calibration and standardization of procedures employed in clinical analysis and for routine critical evaluation of the daily working standards used in these procedures.

Purity	99.9 percent
α -D-Glucopyranose	greater than 99.0 percent
β -D-Glucopyranose	less than 1.0 percent
Moisture	0.06 percent
Ash	0.002 percent
Insoluble Matter	0.001 to 0.006 percent
Nitrogen	less than 0.001 percent

Specific Rotation

$$[\alpha]_D^{20} = +53.2^\circ \text{ (at equil., c 20.1 in water)}$$

$$[\alpha]_{546}^{20} = +62.8^\circ \text{ (at equil., c 20.1 in water)}$$

$$[\alpha]_D^{20} = +112.6^\circ \text{ (initial, c 10.05 in methyl sulfoxide)}$$

The value for the purity has an estimated inaccuracy of ± 0.1 percent.

The D-glucose used for this standard reference material was obtained from Pfanstiehl Laboratories, Inc., of Waukegan, Illinois. Analyses were performed by R. F. Brady, Jr., B. Coxon, M. M. Darr, T. E. Gills, E. C. Kuehner, R. A. Paulson, T. C. Rains, T. A. Rush, W. P. Schmidt, J. H. Thomas, and W. L. Zielinski of the Analytical Chemistry Division.

The overall direction and coordination of technical measurements leading to the certification were under the chairmanship of R. Schaffer.

The technical and support aspects concerning the preparation, certification, and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by T. W. Mears.

Washington, D. C. 20234
November 18, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

Certificate of Analysis

Standard Reference Material 918

Potassium Chloride

(Clinical Standard)

This standard reference material is certified for use in the calibration and standardization of procedures employed in the determination of potassium and chloride ions in clinical analyses. The sample consists of highly purified potassium chloride. Chemical assay as well as analyses for specific impurities indicate that the material may be considered essentially pure, except for moisture due to occlusion.

Purity 99.9 ± 0.0 percent

The above value for the purity of the material is based on a sample dried over magnesium perchlorate for 24 hours. Potassium chloride is hygroscopic when the relative humidity at room temperature exceeds 75 percent, but can be dried to the original weight by desiccation over freshly exposed P_2O_5 or $Mg(ClO_4)_2$ for 24 hours. The material should be stored with such a desiccant. The potassium was determined by a combination of gravimetric and isotope dilution analyses. More than 99 percent of the potassium was precipitated, filtered, and weighed as potassium perchlorate. The weight of potassium perchlorate was corrected for rubidium perchlorate. The soluble potassium was determined by isotope dilution mass spectrometry. Total potassium was the sum of the potassium from the potassium perchlorate and the potassium from the filtrate. The chloride was determined by a coulometric argentimetric procedure.

Based on 12 independent measurements for each ion, the sample was considered homogeneous. Material dried at $500^\circ C$ for 4 hours in a platinum or Vycor crucible (Pyrex is unsatisfactory) was assayed at 99.98 ± 0.01 percent. The loss of moisture by this procedure was about 0.07 percent.

The potassium chloride used for this standard reference material was obtained from the J. T. Baker Chemical Company, of Phillipsburg, New Jersey. Analyses were performed by G. Marinenko, T. J. Murphy, T. C. Rains, T. A. Rush, W. P. Schmidt, and V. C. Stewart.

The overall direction and coordination of technical measurements leading to the certification were under the chairmanship of W. R. Shields.

The technical and support aspects concerning the preparation, certification, and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
January 22, 1971

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

Certificate of Analysis

Standard Reference Material 984

Rubidium Chloride

RbCl, rubidium assay, weight percent 99.90 ± 0.02
Absolute abundance ratio, $^{85}\text{Rb}/^{87}\text{Rb}$ 2.593 ± 0.002

This lot of rubidium chloride was prepared to ensure material of intermediate purity and high homogeneity. The material is somewhat hygroscopic, absorbing approximately 0.6 percent moisture in a 75 percent relative humidity at room temperature, but can be dried to the original weight by desiccation over freshly exposed P_2O_5 or $\text{Mg}(\text{ClO}_4)_2$ for twenty-four hours. The material should therefore be stored with a desiccant such as P_2O_5 .

The assay of this material is based on the determination of rubidium by a combination of gravimetry and isotope dilution analysis on eight samples of about 2 g each of the dried RbCl. More than 99% of the rubidium was precipitated, filtered and weighed as rubidium perchlorate. The weight of RbClO_4 was corrected for potassium and cesium perchlorate. The soluble rubidium was determined by isotope dilution mass spectrometry. The total rubidium was the sum of the rubidium from the rubidium perchlorate and the rubidium from the filtrate. All weighings were corrected to vacuum and the atomic weights used in the calculations were from the 1969 Table of Atomic Weights. The indicated tolerance is at least as large as the 95 percent confidence level for a single determination.

Chloride was determined by silver coulometry to be 29.32 weight percent. Preferential oxidation of iodide and bromide showed that the material contains $<0.001\%$ I and $<0.003\%$ Br. Flame emission spectrometry indicated lithium, <0.02 ppm; sodium, 2.3 ppm, potassium, 420 ppm; and cesium 24 ppm. Emission spectrographic examination indicated, in addition, calcium, <10 ppm; magnesium, <10 ppm; silicon, <10 ppm, and aluminum, detection questionable. The loss on ignition at 500°C (20 hours) was 0.010% and the insoluble matter was 0.0001%. A materials balance shows that 99.99 ± 0.02 weight percent of the material is accounted for.

The absolute abundance ratio of $^{85}\text{Rb}/^{87}\text{Rb}$ was determined by triple-filament solid-sample mass spectrometry. Mixtures of known $^{85}\text{Rb}/^{87}\text{Rb}$ ratio, prepared from nearly isotopically pure separated rubidium isotopes, were used to calibrate the mass spectrometers. The indicated uncertainties are overall limits of error based on 95 percent confidence limits for the mean and allowances for the effects of known sources of possible systematic error. Details of the preparation and measurements are described in a published paper [J Res NBS, 73A, 511-516 (1969)].

The following members of the Analytical Chemistry Division contributed to the characterization of this material: T. J. Murphy and P. J. Paulsen - rubidium assay; G. Marinenko - chloride assay; T. C. Rains and T. A. Rush - flame emission determinations; E. K. Hubbard - emission spectrographic analysis; and E. J. Catanzaro and E. L. Garner - absolute ratio determination.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects involved in the preparation, certification, and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
July 27, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

Certificate of Analysis

Standard Reference Material 1061c

Magnesium Cyclohexanebutyrate

(Standard for Determination of Magnesium in Petroleum Products)

This compound was prepared to ensure material that is essentially free from other metals and has suitable solubility, compatibility, and uniformity for use in the preparation of a standard of magnesium in lubricating oils.

CHEMICAL AND SPECTROGRAPHIC ANALYSES

Procedure and Results of Chemical Analysis

Magnesium, percent 6.45 ± 0.02

The uncertainty shown represents the 95 percent confidence limit of the mean based on twelve determinations and allowances for the effects of known sources of possible errors.

Magnesium was determined by wet-ashing a 1-g sample (dried for 48 hr over phosphorus pent-oxide) with sulfuric and nitric acids, precipitating twice with diammonium hydrogen phosphate, and weighing the $Mg_2P_2O_7$ after ignition at $1050^\circ C$.

Procedure and Results of Spectrographic Analysis

The compound was examined spectrographically for metallic impurities. A 5-mg sample of the compound was excited in a direct current arc and the photographed spectrum was examined for the characteristic lines of 51 elements. No significant impurities were found.

STABILITY: Tests show that standard lubricating-oil solutions of this compound with concentrations of magnesium up to 500 ppm are stable for several weeks when prepared by the directions given on the reverse side of this certificate.

The magnesium cyclohexanebutyrate was prepared by the Eastman Kodak Company of Rochester, N. Y. Chemical analyses were conducted by R. K. Bell and spectrographic analyses by V. C. Stewart.

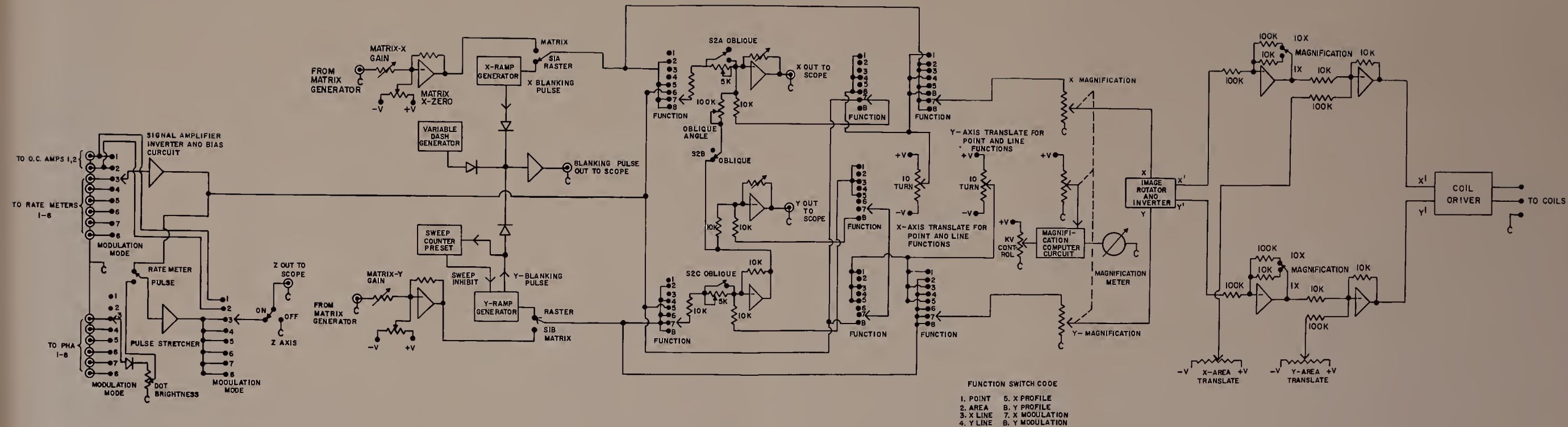
The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of P. D. LaFleur.

The technical and support aspects involved in the preparation, certification, and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by T. W. Mears.

Washington, D. C. 20234
September 9, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

FUNCTIONAL BLOCK DIAGRAM
OF
ELECTRON BEAM SCANNING SYSTEM



U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET		1. PUBLICATION OR REPORT NO. NBS TN-582	2. Gov't Accession No.	3. Recipient's Accession No.
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15. SUPPLEMENTARY NOTES				
16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.) Spectrochemical research activities, improvements in equipment and applications, especially to the certification of NBS Standard Reference Materials, are summarized. In optical emission spectroscopy, studies have been carried out on a modified gas-sheath arc excitation source. Application has been made of this source and several other conventional excitation sources to analytical problems related to both standard reference materials and other materials being investigated at NBS. Newly derived computation procedures for quantitative x-ray fluorescence analysis are described as well as new instrumentation added for x-ray spectrochemical studies. In electron probe microanalysis, research and new instrumentation has been directed to improved detection limits and quantitation; special emphasis has been given to methods for small particles and biological thin cuts. Methods of pre-concentration of impurities have been advanced and applied, in some cases at parts per billion (10^{-9}) limits, to water pollution, river sediment specimens. Mercury, cadmium, and lead were among the elements determined. Work on Standard Reference Materials resulted in certification of several special steels, several high temperature alloys, a high-silicon steel and a titanium alloy, among others. Listings are given of 8 publications and 25 talks by members of the Section during the year.				
17. KEY WORDS (Alphabetical order, separated by semicolons) Analysis; computer program; electron probe; microanalysis; optical spectrometry; pre-concentration techniques; spectrochemical analysis; standard reference materials; x-ray fluorescence				
18. AVAILABILITY STATEMENT analysis. <input checked="" type="checkbox"/> UNLIMITED. <input type="checkbox"/> FOR OFFICIAL DISTRIBUTION. DO NOT RELEASE TO NTIS.			19. SECURITY CLASS (THIS REPORT) UNCL ASSIFIED	21. NO. OF PAGES 126
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